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BORDEAUX MIXTURE: I. PHYSICO-CHEMICAL STUDIES

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WITH PLATES VII AND VIII AND THREE FIGURES IN THE TEXT

I. INTRODUCTION

St. John tells us that in Burgundy and Switzerland the vines bordering the road-side are commonly "smeared with something resembling white lime which children are assured is a deadly poison,"[1] and further remarks, thus indicating that this caution was not a vain one, "that two children were recently killed at Foix by eating poisoned grapes by the way-side."[2] There seems to be little room for doubt but that the substance "resembling white lime" with which the vines along the highways and by-ways were covered was a mixture of lime and copper sulphate very similar to the compound Millardet saw on the grape-vines of St. Julien in the autumn of 1882. This compound, so the manager of Chateau Beaucaillou informed Millardet, was daubed on the vines for the purpose of discouraging thieving, and had been so used from time immemorial in the Gironde. Millardet, however, saw that the mixture served more than this purpose. To use his own words:

"Towards the close of October, 1882, having the opportunity of passing through the vineyards of St. Julien in Medoc, it was not without surprise I noticed that the vines bordering both sides of the road I followed still bore leaves, while everywhere else they had long since fallen. There had been downy mildew that year, so I immediately thought that the persistence of the foliage on the vines bordering the road must be due to some kind of treatment that had protected them from infection. An examination of the foliage confirmed this impression, as the upper surface of the leaves was freely covered with a thin coating of a bluish white pulverulent and adhesive substance.

"Having reached Chateau Beaucaillou I questioned the manager, M. Ernest David who informed me that it was customary in Medoc to cover the leaves towards maturation either with verdigris or a mixture of lime

[1] St. John, J. A. Manners and customs of ancient Greece. 1842.

[2] Loc. cit.

and copper sulphate to discourage thieves, who seeing the leaves copper stained do not dare eat the fruit hidden beneath for fear that it has been similarly soiled."[3]

The wash Millardet saw on the vines of St. Julien was destined to become, owing to his initiative, widely known within a few years under the name of Bordeaux mixture. The wash used by David was the prototype of Millardet's first mixture which, like it, was so thick that it had to be applied by dipping a whisk broom in the mixture and then shaking it over the vines. As first used Bordeaux mixture contained:[4]

	parts
Copper sulphate	5.71
Quicklime	10.71
Water to make	100

But as the above mixture was very inconvenient to use it was promptly modified more or less profoundly, Mach[5] being one of the first to experiment with numerous modifications of the original formula. No material advance was made, however, until 1887, when Millardet and Gayon[6] recommended for general use, and in the replacement of the formula published by the senior author in 1885 (vide supra), a Bordeaux mixture of the following composition:

	parts
Water	100
Copper sulphate	3
Quicklime	1

and for trial the two following formulae:

	A *parts*	B *parts*
Water	100.0	100.0
Copper sulphate	2.0	1.0
Quicklime	0.67	0.34

[3] Millardet, A. Traitement du mildiou et du rot. Journ. d'agr. pratique II: 572. 1885.

Traitement du mildiou et du rot, p. 16, Bordeaux, 1886.

[4] Millardet, A. Annales Soc. Agr. Gironde. 1885.

The mixture was prepared as follows: First, 8 kilos copper sulphate were dissolved in 100 litres water; secondly, 15 kilos quicklime were slacked with 30 litres water and added to the solution of copper sulphate. Allowing for the proper increases in volume this gives a mixture of the above strength in per cent. I should mention, however, that the mixture is usually spoken of by the authors of the day as containing 6% copper sulphate and 12% quicklime.

[5] Mach E. Bericht über die Ergebnisse der im Jahre 1886 ausgefuhrten Versuche zur Bekämpfung. Bozen, 1887.

[6] Millardet, A. and Gayon, U. Les divers procédés de traitement du mildiou par les composés cuivreux. Journ. agr. pratique I: 704. 1887.

At the present day, in France and Switzerland, Bordeaux mixtures are made so as to contain 2% to 3% copper sulphate though the quantity of quicklime used varies from an amount just sufficient to produce alkalinity up to a quantity equal to that of the copper sulphate taken. In the Rheingau a Bordeaux mixture containing 0.5% copper sulphate and 1% quicklime appears to be somewhat extensively used.[7] In Italy, Cavazza, as long ago as 1886, advocated the use of a Bordeaux mixture containing 0.6% copper sulphate and prepared with lime water, the quantity taken being sufficient to produce a neutral mixture. Cavazza's formula, however, appears not to have been extensively used, for while Savastano[8] states that the strength in copper sulphate of the Bordeaux mixtures used in Italy varies between 0.5% and 1%, he does not mention lime water as being used in the preparation of the 0.5% mixture. In the United States the Bordeaux mixture used is very variable in composition. It may contain all the way from 0.5% to 1.6% copper sulphate, the amount of quicklime used being exceptionally less than the copper sulphate, more often in equal amounts, not infrequently in greater amounts, especially in those mixtures that contain less than 1% copper sulphate. In the other countries of the world the Bordeaux mixtures used belong either to the European or American types, if one may so say.

It is thus apparent that during the twenty-seven years that have elapsed since Bordeaux mixture was first introduced very little or no progress has been made towards standardizing the mixture, for a perusal of the literature does not warrant the assumption that the profusion of formulae, both as regards strength in copper sulphate and ratio copper sulphate to lime, have a biological significance. Regarding the strength and composition of Bordeaux mixture there are almost as many opinions as there are writers. Furthermore, the tendency amongst authors towards regional types of formulae reminds one of the old saying: "verité en deça des Pyrenées, erreur au dela." In the following table these facts are clearly brought out, and one can also recognize without difficulty the European and American formulae.

Not only is there a marked divergence of opinion regarding the composition of Bordeaux mixture, but a perusal of the literature makes it quite clear that, as regards the chemical and physical properties (particularly the latter) of the mixture, authors are by no means agreed, and, as a consequence, its toxic and other biological properties are also very imperfectly understood. As, however, a knowledge of the chemical and physical properties of Bordeaux mixture is a necessary preliminary to a

[7] Bayer, L. Beitrag zur pflanzenphysiologischen Bedeutung des Kupfers in der Bordeaux-brühe, Thesis. Konigsberg, 1902.

[8] Savastano, L. Patologia arborea applicata. Naples, 1910.

TABLE I

Strength of Bordeaux mixtures in terms of copper sulphate, and corresponding ratios copper sulphate to quicklime recommended by different authors

PER CENT COPPER SULPHATE	RATIO COPPER SULPHATE TO QUICKLIME RECOMMENDED			
3.00	4:1	3:1	3:2	1:1
2.00	4:1	3:1	2:1	1:1
1.80	36:25			
1.60	16:11	1:1		
1.50	5:3	3:2	1:1	
1.25	125:71	1:1	5:6	
1.00	3:1	1:1	2:3	
0.80	1:1			
0.75	1:1	13:25	13:45	
0.64	5:1			
0.625	1:1			
0.60	2:5			
0.50	1:1	5:6	4:5	

study of its biological properties it has seemed to me that such a study might be undertaken profitably even by a botanist. In the present paper, therefore, I will confine my attention strictly to the subject matter of the title. When we have a better knowledge of the chemistry and physics of Bordeaux mixture the biological studies which are so attractive to physiologists and pathologists alike will no longer present the difficulties which they now do.

II. CHEMISTRY OF BORDEAUX MIXTURE

The reactions which take place when lime water or milk of lime is added to a solution of cupric sulphate are somewhat complex, and, in consequence, a certain lack of agreement is found to exist between the various authors who have studied the chemistry of Bordeaux mixture.

According to Millardet and Gayon,[9] Chester,[10] and the majority of writers on the subject, the reaction that takes place when cupric sulphate and milk of lime, or lime water are brought together results in the formation of cupric hydroxide and calcic sulphate, calcic hydrate being also present when the lime water, or milk of lime is used in excess. The following formula represents the reactions involved when calcic hydrate is used in just sufficient quantity to satisfy the reaction:

$$CuSO_4 + Ca(OH)_2 + H_2O = Cu(OH)_2 + CaSO_4$$

[9] Millardet, A. and Gayon, U. Traitement du Mildiou par le mélange de sulfate de cuivre et de chaux. Journ. agr. pratique II: 709. 1885.

[10] Chester, F. D. The copper salts as fungicides. Journ. Mycology. **6:** 22. 1891.

The cupric sulphate calcic oxide[11] ratio satisfying the above reaction is 1:0.224.

While the predominant opinion amongst writers has been and is that cupric hydrate is precipitated when calcic hydrate is added to a solution of cupric sulphate, other views have been held and are held at the present day regarding the nature of the precipitate formed.

In 1887 Millardet and Gayon,[12] while adhering to the view that cupric hydrate is the salt formed in Bordeaux mixture, nevertheless pointed out that the amount of calcic oxide, i.e., 0.224 gram, that is required to completely precipitate 1 gram cupric sulphate in the form of the hydrate would, if the reaction were allowed to continue sufficiently long, precipitate 1.25 grams cupric sulphate. In other words the cupric sulphate and calcic oxide would react in the ratio 1:0.179 which is almost identical, as may be gathered from the researches of Pickering, with that required for the formation of the basic sulphate 5 $CuO.SO_3$.

In 1890 Sostegni[13] studied the reactions involved in the manufacture of Bordeaux mixture, and concluded that the precipitate formed consisted of a mixture of cupric hydrate, basic cupric sulphate, and a double sulphate of lime and copper similar to Lyellite[14] in composition except for the greater amount of calcic sulphate present.

In 1894 Fairchild opined "that the first reactions which take place when milk of lime is slowly added to a solution of copper sulphate are those leading to the formation of the basic sulphates of copper" . . . . but that "when sufficient lime has been added to entirely neutralize the copper sulphate, the resulting compound is an hydroxide of copper $Cu(OH)_2$."[15]

Pickering[16] has shown that basic sulphates are formed by the interaction of metallic sulphates and caustic alkalies, except in the case of manganese

[11] It would be more logical to write the ratio as occurring between the reacting salts, but, as Bordeaux mixture is almost invariably prepared by hydrating at time of preparation a given amount of calcic oxide, the method followed has obvious practical advantages.

[12] Millardet, A. and Gayon, U. Les divers procédés de traitement dû mildiou par les composés cuivreux. Journ. agr. pratique. I: 703. 1887.

[13] Sostegni, L. Sulla composizione chimica della casi detta poltigia bordolese. Le Stazione Sperimentali Agrarie Italiane **19**. 1890.

[14] According to A. S. Dana (Manual of Mineralogy, 6 ed., p. 961. 1892) Lyellite, more properly Langite, is a basic sulphate of copper of the formula 4 CuO. SO_3, 4 H_2O, though calcic sulphate frequently accompanies it.

[15] Fairchild, D. G. Bordeaux mixture as a fungicide. U. S. Dept. Agr. Div. Veg. Path. Bull. 6: 13. 1894.

[16] Pickering, S. U. On the basic sulphates of copper. Chemical News **47**. 1883. The chemistry of Bordeaux mixture. Journ. Chem. Soc. (Transactions) **91**: pt. 2. 1907.

and magnesium when the hydroxide is precipitated. In the other cases, when just enough alkali is added to completely precipitate the metal, a basic sulphate is formed, which, upon the further addition of alkali, converts the salt which was first formed into one or several basic salts, or into the hydroxide. The hydroxides, however, appear to form only when the stronger alkalies (sodium or potassium hydroxide) are used, but not in the case of calcium hydroxide which always precipitates basic sulphates, except when used in very large excess, when a double oxide is formed. In the case of the more caustic alkalies (sodium or potassium), the cupric hydroxide produced is the unstable form which gradually darkens on standing. The color of the precipitate formed by calcium hydroxide, on the other hand, does not change; hence it would appear doubtful that any hydroxide is produced.

According to Pickering [17] the following distinct basic salts may be formed when cupric sulphate is precipitated by calcic hydrate.

$4\ CuO.SO_3$
$5\ CuO.SO_3$
$10\ CuO.SO_3$
$10\ CuO.SO_3,\ 3\ CaO$
$CuO.\ 3\ CaO$

The equations of formation of the above basic salts, excluding CuO. 3CaO which is not of particular interest to the student of Bordeaux mixture, may be written thus:

$$4\ CuSO_4 + 3\ Ca(OH)_2 = 4\ CuO.SO_3 + 3\ CaSO_4$$
$$5\ CuSO_4 + 4\ Ca(OH)_2 = 5\ CuO.SO_3 + 4\ CaSO_4$$
$$10\ CuSO_4 + 9\ Ca(OH)_2 = 10\ CuO.SO_3 + 9\ CaSO_4$$
$$10\ CuSO_4 + 12\ Ca(OH)_2 = 10\ CuO.SO_3, 3\ CaO + 9\ CaSO_4$$

The quantities of cupric sulphate and calcic hydrate required to form the above basic sulphates are as follows:

For $4\ CuO.SO_3$: 6 parts cupric sulphate to 1.32 parts calcic hydrate (1 part calcic oxide).

For $5\ CuO.SO_3$: 5.5 parts cupric sulphate to 1.32 parts calcic hydrate (1 calcic oxide).

[17] Pickering, S. U. The chemistry of Bordeaux mixture. Journ. Chem. Soc. (Transactions) **91.** pt. 2. 1907.

Bordeaux Spraying. Journ. Agr. Science **3:** 171 et seq. 1908–10.

The Constitution of basic salts. Journ. Chem. Soc. (Transactions) **97.** pt. 2: 1851 et seq. 1908.

Bedford, Duke of, and Pickering, S. U. Woburn Experimental Fruit Farm Report, **11:** 25 et seq. 1910.

Woburn Experimental Fruit Farm Report, **8:** 5 et seq. 1908.

For 10 $CuO.SO_3$: 5 parts cupric sulphate to 1.32 parts calcic hydrate (1 part calcic oxide).

For 10 $CuO.SO_3$,3 CaO: 3.71 parts cupric sulphate to 1.32 parts calcic hydrate (1 part calcic oxide).

The basic sulphates 4 $CuO.SO_3$ and 5 $CuO.SO_3$ are somewhat soluble in the mother liquor, the former to the extent of 1 part in 40,000, the latter to the extent of 1 to 2 parts per million.[18] The other basic salts, however, are quite insoluble in the mother liquor though beginning with 10 $CuO.SO_3$ they dissolve with increasing readiness in dextrose,[19] saccharose and other organic substances that give the biuret reaction.

The basic sulphates also show well marked differences when subjected to the action of heat. In the cases of 4 $CuO.SO_3$ and 5 $CuO.SO_3$ the change brought about by boiling is similar to that which occurs in these salts on standing, they become denser and, in the case of 4 $CuO.SO_3$, greener. The basic salt 10 $CuO.SO_3$, on the other hand, turns completely black owing to the formation of cupric oxide, but 10 $CuOSO_3$,3 CaO is not affected. The formation of cupric oxide also occurs to a slight extent in 10 $CuO.SO_3$ and to a marked degree in 1% and 2% neutral Bordeaux mixtures (vide Chap. V for the method of their preparation) when kept at room temperatures though I have not noticed it in the Bordeaux mixtures in which the ratios cupric sulphate to calcic oxide varied between 1:1 and 1:$\frac{1}{4}$. At boiling temperature, however, cupric oxide forms in sufficient amount to be detected by ocular inspection in the following mixtures: 2% (1:1); 1% (1:1); 2% (1:$\frac{1}{2}$); 1% (1:$\frac{1}{2}$); 2% (1:$\frac{1}{4}$); 1% (1:$\frac{1}{4}$); $\frac{1}{2}$% (1:$\frac{1}{4}$) and is absent from the following: $\frac{1}{2}$% (1:1); $\frac{1}{4}$% (1:1); $\frac{1}{8}$% (1:1); and $\frac{1}{2}$% (1:$\frac{1}{2}$). One may therefore conclude that in Bordeaux mixtures made with milk of lime, at least when they have been recently made, the copper is *pro parte* in the form of the basic sulphate 10 $CuO.SO_3$ except in weak mixtures. In the case of Bordeaux mixtures in which the precipitate crystallizes with age, i.e., the washes currently used in practise, no cupric oxide forms on boiling after crystallization is completed, even though 10 $CuO.SO_3$ were present in the freshly made mixtures.

It has also been pointed out[20] that one basic sulphate may be transformed into another by the necessary addition of more copper sulphate or more lime water as the case may be. If we take, for instance, the lowest basic sulphate (4 $CuO.SO_3$) we can by the addition of more lime water obtain any of the higher basic sulphates, or mixtures of basic sulphates. By adding the lime water in the proper successive amounts, we can pass from

[18] Bedford, Duke of, and Pickering, S. U. Woburn Experimental Fruit Farm Report, **11**: 49.

[19] Loc. cit.

[20] Loc. cit.

the dense and rapidly settling 4 $CuO.SO_3$ through a series of gelatinous and slowly settling salts, or mixtures of salts to highly basic compounds, the precipitates of which are dense and settle promptly.

These facts led the Duke of Bedford and Pickering[21] to the conclusion that the changes occurring in Bordeaux mixtures (1:1) prepared with milk of lime are of the same nature as those produced when lime water is used in lieu of milk of lime.

In the Bordeaux mixtures made with milk of lime the change would be gradually towards the formation of the basic sulphate or mixtures of basic sulphates that the ratio cupric sulphate to calcic oxide used in their preparation would indicate. In reality, however, the reactions are not quite so simple. In the first place the physical properties of the copper precipitate formed in a 1:1 Bordeaux mixture made with milk of lime depends on the concentration of the mixture in cupric sulphate. In mixtures containing from 0.25% to 6% cupric sulphate the gelatinous precipitate first formed becomes, after a relatively short time, crystalline, the copper salt being then in the form of blue sphaerocrystals which suffer no further change when preserved in the mother liquor. This occurs despite the fact that an abundance of calcic hydrate yet remains which should result in a slow but continuous change of the copper precipitate.

In the second place it should be pointed out that the formation of sphaerocrystals occurs also in Bordeaux mixtures in which the ratio cupric sulphate to calcic oxide is 1:0.5 but apparently only in mixtures containing more than 0.25% cupric sulphate. On the other hand no sphaerocrystals are formed in mixtures in which the ratio cupric sulphate to calcic oxide is 1:0.25 or greater, even when the percentage of cupric sulphate used in making the mixture ranges between 0.5% and 2%. The formation of the sphaerocrystals seems to be definitely limited, first by the strength of the mixture in cupric sulphate, and second by the ratio cupric sulphate to calcic oxide. The view, therefore, that the changes occurring in Bordeaux mixtures made with milk of lime are homologous to those obtainable by precipitating cupric sulphate with lime water does not seem justifiable. The sphaerocrystals formed in Bordeaux mixtures made with milk of lime are probably chemically distinct from the basic sulphates studied by Pickering;[22] nor is it probable that they are similar in composition to those observed by Sostegni during the course of his studies on Bordeaux mixtures and considered by him as being a double salt of copper and lime resembling Lyellite.

As the lack of adhesiveness and rapid settlement of Bordeaux mixtures made with milk of lime is due to the formation of the above mentioned

[21] Loc. cit.

[22] Loc. cit.

sphaerocrystals, the factors affecting their development are of sufficient importance to warrant careful study.

The factors influencing the formation of the sphaerocrystals, in other words the keeping quality of Bordeaux mixtures, are: concentration, temperature, ratio cupric sulphate to calcic oxide, presence of foreign substances in the cupric sulphate, or in the calcic oxide. The addition of substances not found in the cupric sulphate or calcic oxide may also affect the keeping quality of the mixtures.

The effect of concentration, temperature, and ratio cupric sulphate to calcic oxide are so intimately related that, while at first sight it would appear simplest to consider them under separate captions, such a treatment can not be advantageously undertaken. I will, therefore, consider under *A* these dependent factors together, and under *B* the effect of foreign substances on the rate of formation of the sphaerocrystals.

A. The point of complete deterioration of Bordeaux mixtures may be determined in several ways. For instance, color may be used for this purpose, deteriorated mixtures differing in this respect quite markedly from fresh mixtures, as has been pointed out by the Duke of Bedford and Pickering.

The rate at which Bordeaux mixtures settle may also be taken as an indication. It is, however, impossible to determine by coloration, or rate of settlement when the gelatinous magma first formed is completely replaced by sphaerocrystals. Some more accurate method of determining this point is, therefore, needed, and I have found the following to satisfy the conditions required:

A drop of the Bordeaux mixture to be tested is placed on a microscopic slide, rapidly dried, and cooled; a drop of fresh hydrogen sulphide is then placed on the mixture when the presence or absence of gelatinous magma can be readily brought out by microscopic study. It should, however, be noted that when the sphaerocrystals are forming they are more readily acted upon by hydrogen sulphide water and will dissolve to some extent, forming a gelatinous magma indistinguishable from that formed by the interaction of the cupric sulphate and calcic hydrate. Bordeaux mixtures that have not entirely gone bad will, therefore, appear more gelatinous than they really are. When, however, one is not desirous of knowing exactly the state of the mixture at a given time, but only the point of complete deterioration, this method satisfies the conditions required and was used by me in obtaining the data given in the following pages.[23]

[23] If greater accuracy is required, the drop of Bordeaux mixture must be dried and then subjected to the action of gaseous hydrogen sulphide. When so treated the copper precipitate remains unchanged. Potassium ferrocyanide does not give satisfactory results, and when used with acetic acid "Traube cells" not infrequently mycelloid in character develop freely.

To take up first the effect of the concentration of Bordeaux mixtures (1:1) on their keeping quality. When one prepares a series of Bordeaux mixtures (1:1) in which the strengths in cupric sulphate are 0.125%, 0.25%, 0.5%, 1%, 2%, 4% and 6% he will note that within the temperature 9°C. and 30°C. sphaerocrystals appear in all the mixtures except the 0.125% in which they do not even develop after long standing; the 0.125% cupric sulphate mixture behaves similarly to mixtures of like strength made with lime water. At a concentration of 0.25% cupric sulphate, as also in the stronger mixtures, the change is radical, and, in a comparatively short time, the gelatinous copper precipitate first formed (Plate 8, figs. 1 and 2) disappears, and is replaced by a mass of the blue sphaerocrystals above mentioned (Plate 8, fig. 3).

The rate at which these sphaerocrystals form depends both on the concentration and temperature of the mixtures. At a temperature of 9°C. the various mixtures exhibit marked characteristics which tend to disappear at higher temperatures. At 9°C., 2% Bordeaux mixture (1:1) deteriorates much more slowly than mixtures stronger or weaker in cupric sulphate. One-half per cent Bordeaux mixture on the other hand deteriorates more rapidly than either 0.25% or 1% mixtures. At a temperature about 25°C., the 1%, 0.5% and 0.25% mixtures deteriorate in approximately the same time, but the other mixtures crystallize at about the same relative rate that they do at 9°C.

The general results I have obtained are shown in the following table:

TABLE II

Effect of concentration and temperature on rate of deterioration of 1:1 Bordeaux mixtures

STRENGTH OF MIXTURE IN CUPRIC SULPHATE	TIME REQUIRED FOR DETERIORATION	
	At temperature 9°C.	At temperature 25°C.
per cent	*hours*	*hours*
6.0	96	
4.0	144	16
2.0	264	21
1.0	192	5
0.5	72	5
0.25	336	8
0.125	∞	∞

Bordeaux mixtures in which the ratio cupric sulphate calcic oxide is 1:0.5 behave similarly to 1:1 mixtures. The 0.125% mixtures change little or not at all with age while after a certain lapse of time the precipitate in mixtures containing from 0.5% to 6% cupric sulphate is made up of blue sphaerocrystals that are apparently identical with those formed in

1:1 mixtures. The rate of deterioration of 1:0.5 mixtures, however, is not at all points similar to that of 1:1 mixtures. In the case of the former the 0.5% mixtures deteriorate most slowly instead of most rapidly; whereas in the case of the latter the 2% mixtures deteriorate most slowly. Mixtures in which the ratio cupric sulphate to calcic oxide is 1.05 also become crystalline more slowly than those in which the ratio is 1:1, as will appear from the following table in which the rates of deterioration of both types are given *en regard*.

While the Duke of Bedford and Pickering[24] were apparently the first to point out that Bordeaux mixtures as usually prepared, i.e., with excess

TABLE III

Effect of concentration on rate of deterioration of 1:1 and 1:0.5 Bordeaux mixtures

STRENGTH OF MIXTURE IN CUPRIC SULPHATE	RATIO CUPRIC SULPH. / CALCIC OXIDE	TIME REQUIRED FOR DETERIORATION AT TEMPERATURE 9°C.
per cent		*days*
6.0	1:1	4
6.0	1:0.5	5
4.0	1:1	4
4.0	1:0.5	5
2.0	1:1	8
2.0	1:0.5	10
1.0	1:1	7
1.0	1:0.5	8
0.5	1:1	3
0.5	1:0.5	14
0.25	1:1	7
0.25	1:0.5	∞
0.125	1:1	∞
0.125	1:0.5	∞

lime, deteriorated rapidly, it has nevertheless been very generally mentioned in the literature that the mixtures should be used fresh. The data above given shows that not only should Bordeaux mixtures be used fresh, but that heretofore not sufficient emphasis has been laid on this fact.

B. The effect of foreign substances on deterioration. I will take up first the effect of foreign substances in the calcic oxide and cupric sulphate on the rate of deterioration.[25]

Three substances are commonly found in burnt limes: magnesic oxide, magnesic carbonate, and calcic carbonate. Of these three substances calcic carbonate appears to be without effect on the rate of deterioration

[24] Loc. cit.

[25] In those experiments on the effect of foreign substances on the rate of deterioration of Bordeaux mixtures, I have used 1% mixtures (1:1) in which 5%, 10%, or 15% of the calcic oxide or cupric sulphate as the case might be, was replaced by the impurity added.

even when used to the extent of 15%. In the case of magnesic carbonate, deterioration is retarded very considerably, even when as little as 5% of the salt is used, and 10% and 15% are very much more effective. Magnesic oxide, on the other hand, even while retarding deterioration markedly, especially at the higher concentrations (10% to 15%), is not as efficient as magnesic carbonate. In fact, of all three substances, the latter is by far the most valuable.

In commercial cupric sulphate, ferrous sulphate is the only impurity of any importance commonly met with, but even at a strength of 15% it does not noticeably retard the deterioration of the mixtures. It should, however, be noted that while as little as 5% ferrous sulphate is sufficient to mask the color of the copper precipitate in fresh Bordeaux mixture, as soon as crystallization has occurred, the wash resembles any other deteriorated mixture.[26] When, on the other hand, a Bordeaux mixture contains 15% ferrous sulphate the color of the precipitate always betrays the presence of iron.

I have gathered together in the following table the data I have obtained on the influence of impurities in the cupric sulphate, or calcic oxide on the crystallization of Bordeaux mixture.

TABLE IV

Effect of impurities in the cupric sulphate, and calcic oxide on the rate of deterioration of 1% Bordeaux mixtures (1:1). Rate of deterioration in relative numbers

WITNESS	CALCIC CARBONATE			MAGNESIC CARBONATE			MAGNESIC OXIDE			FERROUS SULPHATE		
	5%	10%	15%	5%	10%	15%	5%	10%	15%	5%	10%	15%
100	100	100	100	160	200	200	160	160	160	100	130	130

Various substances or salts have been added by different investigators to Bordeaux mixture either to increase its adhesiveness, its efficiency, or prevent its deterioration. For the latter purpose Kelhofer[27] has proposed saccharose. For the purposes of increasing adhesiveness or efficiency, or both, certain organic substances, or inorganic salts have been used, the most important of which are: saccharose, glue, ammonic salts, and ferrous sulphate.

We have already seen that ferrous sulphate is of no great value for preventing crystallization, but the other substances above-mentioned have one and all a certain degree of merit. Peptone, plasterers' glue, cabinet workers' glue, ammonic sulphate, ammonic chloride, and saccharose are

[26] Bordeaux mixtures (1:1) containing 10% ferrous sulphate behave similarly.

[27] Kelhofer, W. Ueber einige Gesichtspunkte bei der Herstellung der Bordeauxbrühe. Internationaler phytopathologischer Dienst **1.** 1908.

all capable of retarding crystallization, saccharose being in this respect particularly efficient. A perusal of table V will also show conclusively that organic substances are much more effective preservatives than inorganic salts and what is no less important are usually less active solvents of the copper precipitate the amount of copper in solution being too small to warrant determination. It should, however, not be forgotten that while the substances, or salts capable of retarding crystallization are usually solvents of the copper precipitate, this is not always the case, magnesic oxide and carbonate, for instance, being without action.

TABLE V

Effect of various substances other than impurities in cupric sulphate or calcic oxide on the rate of deterioration at 9°C. of 1% Bordeaux mixtures 1:1

NAME	AMOUNT OF SUBSTANCE USED	RELATIVE TIME FOR CRYSTALLIZATION	COPPER IN SOLUTION AS Cu
	per cent		
Witness		100	none
Saccharose	0.015	not formed[1]	not determined
Peptone	0.005	100	not determined
Peptone	0.01	100	not determined
Peptone	0.02	120	not determined
Peptone	0.04	620	not determined
Peptone	0.08	800	not determined
Glue (cabinet worker's)	0.005	100	not determined
Glue " "	0.01	100	not determined
Glue " "	0.02	100	not determined
Glue " "	0.05	210	not determined
Glue " "	0.10	400	not determined
Glue " "	0.20	?	not determined
Glue (plasterer's)	0.005	100	not determined
Glue "	0.01	100	not determined
Glue "	0.02	120	not determined
Glue "	0.05	620	not determined
Glue "	0.10	800	not determined
Glue "	0.20	?	not determined
Ammonic chloride	0.05	100	not determined
Ammonic chloride	0.10	150	not determined
Ammonic chloride	0.20	180	not determined
Ammonic chloride	0.40	480	0.024%
Ammonic sulphate	0.025	100	not determined
Ammonic sulphate	0.05	160	not determined
Ammonic sulphate	0.10	160	not determined
Ammonic sulphate	0.20	230	not determined
Ammonic sulphate	0.40	230	0.068%

[1] Instead of blue sphaerocrystals cuprous oxide slowly forms.

III. THE WEATHERING OF BORDEAUX MIXTURE

It is generally admitted at the present day that during the process of weathering the copper originally present in insoluble form in the Bordeaux mixture used gradually comes into solution, though the relative importance of the various substances with which it comes in contact is not so well understood. During the process of weathering, Bordeaux mixture is subject to the action of carbon dioxide at all times but particularly in presence of a high relative humidity. It is also subject to the action of water (dew or rain) containing small amounts of carbon dioxide and ammonium salts in solution. The appearance of soluble copper during the weathering of Bordeaux mixture may be the result therefore of the action of the water alone, or of the water plus salts in solution. As, however, the amount of carbon dioxide and ammonium salts meteoric waters contain is quite variable, it is necessary in order to thoroughly understand the action of the weather on Bordeaux mixture, to know what the relative importance of their various components is, and this can best be done by considering them under separate captions.

Water. When an alkaline Bordeaux mixture is allowed to stand exposed to the atmosphere for several weeks, and is then filtered, the toxicity of the filtrate is not appreciably greater than that from a freshly made mixture,[28] the toxicity of which, it may perhaps be well to mention, is not due to copper in any form, but to calcic hydrate. As an alkaline Bordeaux mixture will remain alkaline for a very considerable period, owing to the fact that the exposed surface becomes coated with a film of calcic carbonate, the results obtained by Bayer are exactly what one would expect, for the filtrate from a freshly prepared and an old mixture will contain very nearly if not exactly the same amount of soluble calcic hydrate as the following table shows.

When the excess calcic hydrate is carbonated either by passing carbon dioxide through alkaline Bordeaux mixtures, or by allowing them to dry spontaneously, pure water will dissolve small amounts of copper and the fact can be readily shown in the following manner. A series of slides is sprayed with Bordeaux mixtures in which the ratio cupric sulphate to calcic oxide varies between 5 and 0.5 and is allowed to dry spontaneously and stand at room temperature until carbonated, i.e., twenty-four hours. If drops of water sown with *Phytophthora infestans* or *Plasmopara viticola*[29] spores are now placed upon them, the slides being kept at the optimum temperature for germination (10° to 14°C.) zoospores will form and be set free in the course of two hours or as soon as in sporangia sown in distilled

[28] Bayer. Loc. cit., ante.

[29] Spores of other fungi could undoubtedly subserve the same purpose.

TABLE VI

Per cent soluble calcic hydrate in alkaline Bordeaux mixtures when freshly made, and after standing three weeks at 9°C.

CUPRIC SULPHATE	RATIO CUPRIC SULPHATE / CALCIC OXIDE	RATIO EXPOSED SURFACE / VOLUME	CALCIC HYDRATE IN MIXTURE	
			When fresh	After standing three weeks
per cent			*per cent*	*per cent*
1	1:1	1:2.216	0.140	0.148
1	1:1	1:1.642	0.140	0.148
1	1:1	1:0.384	0.140	0.125
1	1:0.5	1:2.216	0.133	0.0518
1	1:0.5	1:1.642	0.133	0.0037
1	1:0.5	1:0.384	0.133	0.0518
1	1:0.25	1:2.216	0.005	0.0074
1	1:0.25	1:1.642	0.005	0.0055
1	1:0.25	1:0.384	0.005	0.0037

water or tap-water (witnesses) if the mixtures are used at a non-toxic strength.[30] Dr. I. E. Melhus who kindly made the germination tests for me found that Bordeaux mixtures containing 0.5% cupric sulphate were not toxic when tap-water was used, but that when distilled water was employed, no matter what the ratio cupric sulphate to calcic oxide, the mixtures were all toxic at 0.0625% cupric sulphate.

Now the only difference between tap-water and distilled water is that the former contains calcic bicarbonate as well as certain other salts in solution, and as calcic bicarbonate is a precipitant of soluble copper in the electro-positive condition, water containing this salt will be unable to dissolve the copper in Bordeaux mixtures. Clearly then the toxic action of the Bordeaux mixtures is not due to an oligodynamic action of the copper, for, were the copper able to act by its mere presence, the toxicity of the mixtures would not be affected by the water used. Neither can one invoke a solvent action, excretory or otherwise, of the sporangia themselves for, so far as at present known, organic solvents of the copper precipitate of Bordeaux mixtures are more active in alkaline than in neutral mixtures, and their action is not materially interfered with when tap-water is used in lieu of distilled water. The possibility of the sporangia having any solvent action on the copper is, therefore, precluded, and the above experiment may be justly considered as proving that pure water dissolves the copper in carbonated Bordeaux mixtures.

[30] A similar method of demonstrating the presence of soluble copper was used by Millardet and Gayon (vide Recherches nouvelles sur l'action que les preparations cuivreuses exercent sur le peronospora de la vigne. Journ. agr. pratique I: 124. 1887.

While pure water, as we have seen, dissolves small amounts of copper it is not as energetic a solvent as either carbon dioxide or the ammonium salts.

Carbon dioxide. Carbon dioxide not only carbonates the excess calcic hydrate present in alkaline Bordeaux mixtures, but also decomposes the basic copper sulphates. In the case of neutral Bordeaux mixtures, it immediately attacks the basic copper salt, but in the alkaline mixtures the calcic hydrate is first of all carbonated.

The solvent action of carbon dioxide on the copper salts in Bordeaux mixture was apparently first studied by Millardet and Gayon[31] who found that 1 litre of water, saturated with the gas at 15°C. and at atmospheric pressure, dissolved 40 milligrammes cupric hydrate.

The same authors[32] also studied the rate at which copper is liberated from 1.5% Bordeaux mixtures in which the ratios cupric sulphate calcic oxide were 100:21;[33] 100:22.4; 100:44.8; 100:89.6; 100:179.2 and found that when the mixtures were moistened daily with rain-water copper appeared in solution much sooner in neutral than in alkaline mixtures as will appear from the following table.

TABLE VII

Effect of increasing the alkalinity of Bordeaux mixture on the time of appearance of soluble copper

CUPRIC SULPHATE TAKEN	RATIO CUPRIC SULPHATE CALCIC OXIDE	SOLUBLE COPPER PRESENT AFTER
per cent		*days*
1.6	100:21.0	5
1.5	100:22.4	7
1.5	100:44.8	12
1.5	100:89.6	13
1.5	100:179.2	18

Millardet and Gayon have also shown[34] that, when Vitis leaves are sprayed with Bordeaux mixture, the drip from the leaves wet by rain after the wash has become carbonated contains minute amounts of copper,

[31] Millardet, A. and Gayon, U. Traitement du mildiou par le mélange de sulfate de cuivre et de chaux. Journ. agr. pratique II. 1885.

[32] Millardet, A. and Gayon, U. Les divers procédés de traitement du mildiou par les composés cuivreux. Journ. agr. pratique I: 701 et seq. 1887.

[33] The Bordeaux mixture in which the ratio cupric sulphate calcic oxide was 100: 21.0 contained 1.6% cupric sulphate.

[34] Millardet, A. and Gayon, U. Recherches nouvelles sur l'action que les préparations cuivreuses exercent sur le peronospora de la vigne. Journ. agr. pratique I: 124. 1887.

the presence of which can be detected by the behavior of *Plasmopora viticola* sporangia.

Sostegni,[35] who, it will be remembered, considered that the copper in Bordeaux mixture is precipitated as a mixture of the hydrate and a double basic sulphate of copper and lime, believed that the carbon dioxide acted on the basic sulphate which it decomposed forming a copper carbonate and cupric sulphate, the former salt dissolving only to a very slight extent.

Fairchild,[36] on the authority of Willard, wrote the reaction that takes place when carbon dioxide acts on Bordeaux mixture in which the copper is precipitated in the form of a basic sulphate, owing to the use of insufficient calcic hydrate, as follows:

$$2\ (Cu(OH)_2, CuSO_4)+CO_2=2\ CuSO_4+Cu(OH)_2, CuCO_3+H_2O$$

Fairchild also observed that when Bordeaux mixture containing the copper, as he thought, in the form of the hydrate was allowed to dry in air containing carbon dioxide, or when carbon dioxide was passed through the mixture, the presence of soluble copper could be detected by means of potassium ferrocyanide.

Ewert[37] who held the view that the copper in Bordeaux mixture occurs in the form of the hydrate, believed that in 8 to 10 days after the wash was applied, the copper salt became carbonated and soluble in both rain water and water containing carbon dioxide, though to a lesser degree in the former.

Kelhofer[38] found that water containing 0.2% carbon dioxide had a solvent action on the copper precipitate in Bordeaux mixture.

Zucker[39] who used a Bordeaux mixture containing

	parts
Water	100
Cupric sulphate	3
Calcic oxide	1.6

found that 0.0155% copper was dissolved in four hours when carbon dioxide was passed through the mixture.

[35] Loc. cit., ante.

[36] Loc. cit., ante.

[37] Ewert, K. Die fungicide und physiologische Wirkung der Kupperhaltigen Brühen mit besonderer Beruchsichtigung der Bordeauxbrühe. Mitteilungen des Deutschen Weinbau vereines **2**: 244. 1907.

[38] Kelhofer, W. Über die Ausfuhrung und die Ergebnisse von Haftfestigheits versuchen Kupferhaltiger Bekampfungsmittel gegen die Peronospora. Zeitschr. f. Pflanzenkr. **17**. 1907.

[39] Zucker, A. Beitrag zur direkten Beeinflussung der Pflanzen durch die Kupervitriol-Kalkbrühe. Thesis. Stuttgart. 1896.

Schrander[40] studied the rapidity with which copper is liberated from 2% Bordeaux mixtures prepared with varying amounts of lime. This author poured the 2% Bordeaux mixtures into crystallizing dishes, 100 cc. being used in each case. One-half the dishes were kept in the shade, the other half were exposed to the sun, and all were moistened periodically with rain water. The Bordeaux mixtures exposed to the sun dried more rapidly and carbonated more readily than those in the shade. In the case of the neutral Bordeaux mixture soluble copper was detected after twenty-three days, while in the case of the alkaline mixtures (Bordeaux mixtures in which the ratios cupric sulphate to calcic oxide were respectively 1:1 and 1:2) it appeared only in forty-two to fifty-six days. Schrander also examined the drip from the leaves of sprayed plants, for the presence of soluble copper. The drip from the leaves of *Lappa major* and several species of Rheum sprayed with 2% alkaline Bordeaux mixture only gave a reaction for soluble copper after eight to ten days; whereas the drip from the leaves of *Rheum palmatum* sprayed with neutral Bordeaux mixture contained 0.00001% cupric sulphate after twenty-four hours.[41]

Crandall[42] following Schrander, placed 20 cc. of a 1% Bordeaux mixture (1:1) in each of four crystallizing dishes, all of which were kept in the laboratory, two in diffused light and two in sun light. One of the dishes in diffused light, and one of the dishes exposed to the action of the sun's rays were moistened daily. At the end of sixty-five days, when the experiment was discontinued, no soluble copper could be detected in any of the dishes. Crandall also sprayed two potted apple trees three times with a 1% Bordeaux mixture (1:1). Both trees were then placed in a southerly window and the foliage of one of them was moistened almost daily with cistern water, while the foliage of the other tree was kept dry. At the end

[40] Schrander, R. Über die physiologische Wirkung der Kupfervitriol-Kalkbrühe. Landw. Jahrb. **33**. 1904.

[41] The test used by Schrander for determining the presence of soluble copper seems to me quite untrustworthy. He soaked sections of bean seeds in the suspected fluid for three to twenty-four hours, then, after rinsing in distilled water, transferred them into a weak solution of acetic acid in which a crystal of potassium iodide had been placed.

If the copper were present in the solution tested, it would, according to Schrander's view, be fixed by the starch and would, in coming in contact with the potassium iodide, liberate iodine which would immediately color the starch grains blue. As, however, neutral potassium iodide will color starch blue, the reaction being observed on a test plate, when copper free water is used as the solvent, and no increased sensitiveness of the reaction follows the addition of very small amounts of soluble copper, the results obtained by Schrander may or may not have been due to the presence of soluble copper.

[42] Crandall, C. S. Bordeaux mixture. Illinois Agr. Expt. Sta. Bull. 135. 1909.

of fifty-four days no soluble copper was found in either the moistened, or dry mixture.

Pickering,[43] and later the Duke of Bedford and Pickering,[44] studied at some length the action of carbon dioxide on Bordeaux mixtures, the work of the latter completing and supplementing the former. It will only be necessary, therefore, for me to consider the facts presented in the Eleventh Report of the Woburn Experimental Fruit Farm. The Duke of Bedford and Pickering found that the copper was rendered soluble more rapidly and in larger amounts when carbon dioxide was passed through Bordeaux mixtures prepared so as to contain either 4 $CuO.SO_3$ or 10 $CuO.SO_3$ than when it was bubbled through alkaline mixtures containing a large excess of calcic hydrate. The results they obtained are summarized in the following table.

TABLE VIII

Action of carbon dioxide on Bordeaux mixtures of different degrees of alkalinity[45]

BORDEAUX MIXTURE USED	CUPRIC SULPHATE PRESENT AS Cu	AT BEGINNING	SOLUBLE COPPER IN SOLUTION AFTER								AVERAGE OF
			30 min.	2 hrs.	24 hrs.	48 hrs.	72 hrs.	96 hrs.	120 hrs.	192 hrs.	
	per cent										*expts.*
4 CuO. SO_3.	0.16	not det.	0.0288	0.0384	0.0448	0.0608	0.0560	0.0480			4
10 CuO. SO_3.	0.4	not det.	0.0280	0.052	0.08	0.092	0.096	0.096			1
Bordeaux mixture 1:1 fresh..	0.4	0	0	0	0.0016	0.0108	0.0124	0.0124	0.008		3
Bordeaux mixture 1:1 old...	0.4	0	0	0	0.0012	0.0044		0.0008			1
Bordeaux mixture 1:2.....	0.4	0	0	0	0	0.0108	0.0108	0.0088	0.008		1

The basic sulphates of copper when acted on by carbon dioxide should theoretically yield definite amounts of cupric sulphate. The reactions being for the Bordeaux mixtures mentioned in the above table.[46]

$$2.5\ (4\ CuO.SO_3)+3.75\ CO_2=3.75\ (CuO)_2\ CO_2+2.5\ CuSO_4,$$

in other words a solubilization of 25% of the cupric sulphate originally taken

$$10\ CuO.SO_3+4.5\ CO_2=4.5\ (CuO)_2CO_2+CuSO_4$$

or a yield of 10% of the cupric sulphate taken.

[43] Pickering, S. U. Bordeaux spraying. Journ. Agr. Sci. **3**.

[44] Bedford, Duke of, and Pickering, S. U. Loc. cit.

[45] Loc. cit., p. 28. In the original the results are given in a different form.

[46] Bedford, Duke of, and Pickering, S. U. Loc. cit., p. 26.

Theoretically, therefore, the amount of copper liberated by the carbon dioxide should have been, had no side reactions occurred, 0.04 grams in all cases, as the quantities of cupric sulphate used in preparing the mixtures had been so chosen as to yield this amount of soluble copper were the reactions exactly as indicated in the above equations. It will be seen, however, that the amount of copper liberated is greater than the equation calls for in the case of 4 $CuO.SO_3$, and less in the cases of 10 $CuO.SO_3$ and the Bordeaux mixtures 1:1 and 1:2. These anomalies are explained by the authors in the following manner: In the case of 4 $CuO.SO_3$ the greater solubility of the copper is supposed to be due to the solution of one of the basic copper carbonates; while the reduction in the solubility of the copper in the case of the higher basic sulphates is imputed to side reactions between the calcic carbonate and the cupric sulphate liberated.

Gimingham[47] has also observed that carbon dioxide has a markedly solvent action on Bordeaux mixtures, but at the same time notes that the copper rendered soluble by passing carbon dioxide through them, is almost completely reprecipitated when the gas is allowed to disappear spontaneously, or is removed by stirring and shaking, or passing air through the solution. The results obtained by Gimingham[48] were as follows.

Carbon dioxide was blown through Bordeaux mixture containing the basic sulphate 10 $CuO.SO_3$ for twenty-five minutes, when 0.02% soluble copper had passed into solution. Aliquot parts of the mixture were then taken, and treated as follows:

	per cent soluble copper
1. Air blown through mixture for twenty minutes	0.00065
2. Air blown through mixture for forty-five minutes	0.0000
3. Mixture placed in an open beaker and frequently stirred and shaken for one hour.	0.0042
4. Mixture placed in an open beaker and frequently stirred and shaken for twenty-four hours.	0.0000
5. Mixture placed in an open beaker, undisturbed, for one hour	0.015
6. Mixture placed in an open beaker, undisturbed, for twenty-four hours	0.0072

Gimingham offers tentatively the following explanation for the action of carbon dioxide, on Bordeaux mixtures. When carbon dioxide acts on the basic sulphate 4 $CuO.SO_3$, the salt is decomposed with the formation of cupric sulphate and basic cupric carbonate agreeably to the view of Pickering, but that when the carbon dioxide is removed the cupric sulphate is reprecipitated by the basic carbonate, possibly by adsorption.

[47] Gimingham, C. T. The action of carbon dioxide on Bordeaux mixtures. Journ Agr. Sci. **4**. 1911.

[48] Loc. cit., p. 71.

This author, for instance, found by experiment that a small amount of basic carbonate was capable of removing from carbon-dioxide-free-water all but 0.0001% of the cupric sulphate present in a 0.015% solution. On the other hand, when carbon dioxide acts on a more basic sulphate, 10 CuO. SO_3 for instance, the cupric sulphate first liberated combines with the basic carbonate to form a lower basic sulphate and so on until 4 CuO.SO_3 is produced when the reactions are as already indicated.

Besides carbon dioxide, meteoric waters also contain more or less ammonium salts, rain water having the average composition of[49]

	parts per million
Ammonium (NH_3)	0.380
Nitric acid (N_2O_5)	0.979

Copper and the copper salts are, as is well known, soluble in ammonia and ammonium salts. A litre of ammonia containing 0.017% ammonium will dissolve at 18°C. 1.06 grams of cupric hydrate,[50] and, according to Kelhofer,[51] ammonium nitrate is a more efficient solvent than carbon dioxide.

IV. THE PHYSICAL PROPERTIES OF BORDEAUX MIXTURE

A study of the physical properties of Bordeaux mixture has, aside from a purely scientific interest, considerable practical importance. On the character of the precipitate obtained, when Bordeaux mixture is made, depends to a great extent the adhesiveness and to a lesser extent the efficiency[52] of the mixture. As it is beyond the scope of the present paper to undertake the study of efficiency and adhesiveness it will only be necessary to remark that in order that they may be attained to the highest degree the Bordeaux mixture should form a very gelatinous mixture. In the present chapter, therefore, I propose to study the factors modifying the character of the precipitate formed when cupric sulphate and calcic hydrate react. As Bordeaux mixture may be prepared, however, so as to contain one or the other of several basic copper salts, or a mixture of several basic salts depending on the ratio in which the cupric sulphate and calcic hydrate are combined, it will be necessary for us to study:

1. The physical properties of the basic salts of copper.

[49] Miller, W. H. The amounts of nitrogen as ammonia and as nitric acid, and of chlorine in the rain-water collected at Rothamsted. Journ. Agr. Sci. **1**: 286. 1905–06. Average for table IV, tropical rains excluded.

[50] Dawson, M. H. The nature of ammoniacal copper solutions. Part 3. The solubility of cupric hydroxide in ammoniacal sulphate solutions. Journ. Chem. Soc. (Transactions) **95.** pt. 1, p. 372. 1909.

[51] Kelhofer. Loc. cit.

[52] By efficiency I mean the relative toxicity of the unit of copper (Cu).

2. The effect of the temperature of the solution when the reaction takes place.

3. The strength of the solutes, the manner in which they are combined, and the thoroughness with which they are afterwards stirred.

4. The effect of the impurities commonly found in either the copper sulphate, or quicklime on the character of the precipitate.

The physical properties of the basic salts of copper. When lime water and cupric sulphate are mixed together it will be found that the precipitates formed show, *ceteris paribus*, rather well marked physical differences. When the reagents are poured together in the proper proportions to give 4 $CuO.SO_3$ a light flocculent greenish blue (beryl blue)[53] precipitate forms, which at room temperature changes in the course of twelve hours to a curdy heavy bluish green (mirocline green) precipitate which undergoes no further change even after long keeping. When, on the other hand, one precipitates the copper in the form of 10 $CuO.SO_3$ the precipitate does not change with age in either the matter of color or other physical properties. The precipitate when first formed (and even after long standing), is extremely light, floccoso-gelatinous, and greenish blue (cendre blue). The basic sulphate 5 $CuO.SO_3$ which in composition occupies a position intermediate between 4 $CuO.SO_3$ and 10 $CuO.SO_3$ is a gelatinous greenish blue (calamine blue) precipitate very similar in character to 10 $CuO.SO_3$ in fact it was at one time considered by Pickering[54] as producing, for equal weights of copper taken, a more voluminous precipitate than the former. The basic sulphate 5 $CuO.SO_3$ does not perceptibly change with age.

When first prepared 4 $CuO.SO_3$, 5 $CuO.SO_3$ and 10 $CuO.SO_3$ give precipitates which are all tints of the same color, the depth of color increasing, however, with the basicity of the salt, for equal quantities of copper taken.

We have already seen that according to Pickering[55] the following basic sulphates may be obtained by precipitating cupric sulphate with the appropriate amounts of lime water: 4 $CuO.SO_3$, 5 $CuO.SO_3$, 10 $CuO.SO_3$ and 10 $CuO.SO_3$, 3 CaO. These basic salts show quite well marked differences or similarities, both as regards colors and voluminousness of precipitate when recently made, which differences or similarities do not necessarily persist on standing as I have indicated in the case of several of them.

In the following figure, the relative settlement of the above basic salts

[55] Unless stated to the contrary, the colors given are for Bordeaux mixtures made with lime water and containing $\frac{1}{2}\%$ cupric sulphate.

[54] Pickering, S. U. The interaction of metallic sulphates and caustic alkalies. Journ. Chem. Soc. (Transactions). **91**: pt. 2. 1907.

[55] Pickering, S. U. The constitution of basic salts. Journ. Chem. Soc. (Transactions). **97**: 1852. 1910. See also earlier references.

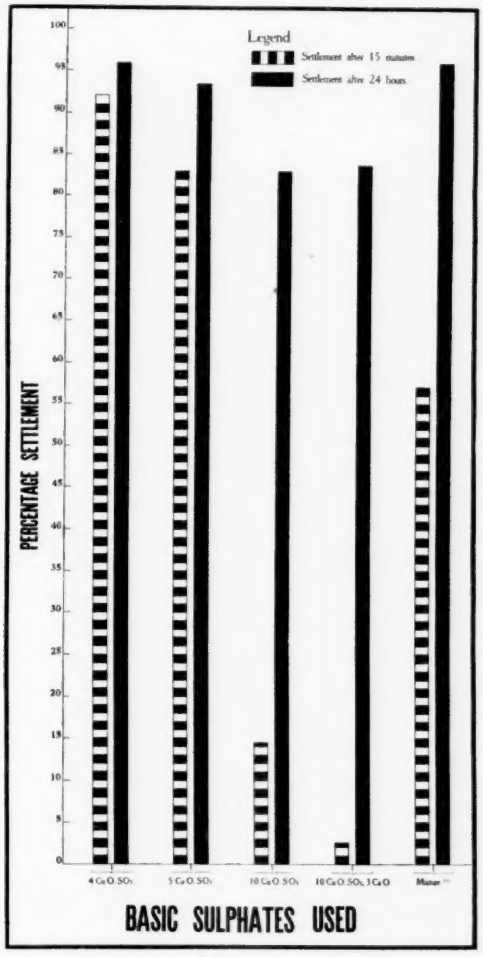

Fig. 1. Relative settlement of basic sulphates containing equal percentages of copper after standing fifteen minutes and twenty-four hours respectively. From the data on page 38 of the Eleventh Report of the Woburn Experimental Fruit Farm.

The above mixture was obtained by combining the cupric sulphate and calcic oxide in the proportions of 3:2 and is composed, according to Pickering, of 10 $CuO.SO_3$, 3 CaO and a more highly basic salt not yet identified.

at time of preparation, and after standing twenty-four hours, is clearly shown, and, in the subjoined table, their colors and color changes.

TABLE IX

Colors[56] *of the basic sulphates of copper* (CuO.2CaO *not included*) *when first prepared and after they have stood for twenty-four hours*

BASIC SULPHATE	CUPRIC SULPHATE TAKEN	COLOR OF PRECIPITATE	
		When fresh	After twenty-four hours
	per cent		
4 CuO. SO_3	0.5	beryl blue	mirocline green
5 CuO. SO_3	0.5	calamine blue	calamine blue
10 CuO. SO_3	0.5	cendre blue	cendre blue
10 CuO. SO_3, 3 CaO.	0.5	bremen blue	calamine blue

The volumes occupied by the different basic sulphates while showing more or less wide differences at first, tend to be more nearly equal after the lapse of twenty-four hours. It will be noticed that the basic sulphates near the sides of the figure resemble one another *ab initio* as well as finally somewhat closely, and the same may be said with equal accuracy of the salts occupying the middle portion. The basic sulphates 4 CuO.SO_3 and 5 CuO.SO_3 are heavy, and the differences between their initial and final volumes are not great; but as the salts become more basic, we notice that the differences between the volumes occupied at first and after twenty-four hours become large. The basic sulphate, 10 CuO.SO_3 forms a very voluminous precipitate as also does 10 CuO.SO_3, 3 CaO the decrease in volume on standing being much more pronounced than in the case of the other basic salts. When the amount of cupric sulphate and lime water are so taken that the ratio cupric sulphate to calcic oxide is 3:2, a rather heavy precipitate is formed which settles rapidly and occupies at the end of twenty-four hours about the same volume as 4 CuO.SO_3. According to Pickering this precipitate is a mixture of 10 CuO.SO_3, 3 CaO and a basic salt not yet identified.

As is shown in table IX the basic sulphates either do or do not change color with age. The great similarity of color between the various basic salts when first made would seem to indicate that one of the higher basic sulphates is always formed first no matter what the ratio in which the

[56] The names of the colors mentioned in the table as well as in the text are taken from Ridgway's Color Standards and Nomenclature, Washington, D. C., 1910, the colors in all cases being viewed on a white ground. The determinations were made for me by Dr. Caroline A. Black to whom I have much pleasure in acknowledging my indebtedness.

cupric sulphate and calcic oxide are brought together, the change to a salt of lower or higher basicity only taking place after a lapse of time. This view was at one time held by the Duke of Bedford and Pickering but was subsequently abandoned.

"The changes[57] occurring after precipitation," they tell us, "suggested that in all cases 10 $CuO.SO_3$ was the substance formed initially, the whole of the copper not being precipitated at first, but reacting only subsequently with this basic sulphate to form the less basic ones 4 $CuO.SO_3$ and 5 $CuO.SO_3$. But this does not appear to be the case: for on adding lime-water sufficient only to form 4 $CuO.SO_3$ and filtering part of the liquid immediately, and part after one hour, the filtrates were found to contain exactly the same, and very small, amounts of copper in solution in both cases. The changes occurring, therefore, must be due merely to physical changes, or to changes in degree of hydration of the precipitates."

I have repeated the above experiments with the results indicated in the following table.

TABLE X

Soluble copper present in 4 $CuO.SO_3$ when made and after standing twenty-four hours

SUBSTANCE	SOLUBLE COPPER PRESENT		STRENGTH OF SOLUTION IN PER CENT CUPRIC SULPHATE
	After making	After twenty-four hours	
	per cent	*per cent*	
4 $CuO.SO_3$	0.0016	0.0016	0.685

While the figures in the above table appear to conform to those given by the Duke of Bedford and Pickering who tell us that 4 $CuO.SO_3$ is soluble in the mother liquor to a slight extent (0.0025% Cu),[58] I am disinclined to accept them as conclusive evidence that the change in color of Bordeaux mixtures are not indicative of changes in chemical composition. For instance when 4 $CuO.SO_3$ is first made the color changes are very rapid, too rapid to be identified by means of a color chart, the color I have given for the freshly prepared mixture containing more green than does the nascent precipitate. It should also be noted that when freshly made 4 $CuO.SO_3$ is only one tint paler in color than 5 $CuO.SO_3$ but in its final form is a totally different color. Now 5 $CuO.SO_3$ itself dissolves very slightly (one or two parts per million)[59] in the mother liquor, and it can be readily seen that, with the small amounts of soluble copper with which we have to deal, mixtures of 5 $CuO.SO_3$ and 4 $CuO.SO_3$ could pass un-

[57] Woburn Experimental Fruit Farm Report **11**: 40.

[58] Loc. cit., ante, p. 49.

[59] Woburn Experimental Fruit Farm Report **11**: 49.

detected. It would seem to me, therefore, that these changes can hardly be other than chemical, and I venture to explain them in the following manner.

When cupric sulphate is precipitated by milk of lime, a gelatinous magma is produced partly made up of Traube cells containing copper sulphate which thus, *pro tempore*, takes no further part in the reaction. As the mixtures contain an excess of lime, the copper and lime react to give a mixture of higher basic sulphates which are bluer in color than 10 $CuO.SO_3$. However, in the course of twenty-four hours all the copper present comes to react with the lime and we have a lower basic sulphate formed (approximately 10 $CuO.SO_3$). That the reverse reaction does not take place is proved by the fact that the color of the precipitate changes immediately to a deeper blue when alkalinity is reached. We have seen that when cupric sulphate and lime water are combined in such proportions that the ratio cupric sulphate to calcic oxide is 3:1 then a rather heavy precipitate is formed which is, according to Pickering, a mixture of 10 $CuO.SO_3$, 3 CaO and a basic salt of unknown composition. When the ratio cupric sulphate to calcic acid is increased to 1:1 the precipitate obtained is, according to the same authority, still a mixture of 10 $CuO.SO_3$, 3 CaO and the basic salt above referred to. It seems doubtful, however, as I have already pointed out[60] that this mixture is really found in Bordeaux mixtures (1:1) prepared with milk of lime when they contain more than 0.125% cupric sulphate. The basic sulphate, preferably mixtures of basic sulphates, that will be found in Bordeaux mixtures (1:1) when first prepared will depend upon their strength in cupric sulphate, the dilution of the milk of lime, and, lastly, the size of the particles of the calcic hydrate in suspension.

It is probable that if the milk of lime is free from coarse particles that Bordeaux mixtures (1:1) containing 1% or over of cupric sulphate will be composed initially of a mixture of 10 $CuO.SO_3$ and 10 $CuO.SO_3$, 3 CaO. At least this conclusion seems to be justified from the fact that such mixtures are bluer than 10 $CuO.SO_3$ just as 10 $CuO.SO_3$, 3CaO is bluer in appearance than 10 $CuO.SO_3$, whereas if the washes contained a mixture of 10 $CuO.SO_3$ and 5 $CuO.SO_3$ they would be paler in color than 10 $CuO.SO_3$, as calamine blue, the color of 5 $CuO.SO_3$, is a tone paler than cendre blue, the color of 10 $CuO.SO_3$. As will be seen from the following table, the colors of Bordeaux mixtures 1:1 are not only bluer to the eye but occur in the same chromatic scale as those of the basic sulphates 10 $CuO.SO_3$ of corresponding strengths in cupric sulphates. I should note that the color of 10 $CuO.SO_3$, 3CaO is the same tone in the broken color that the color of 10 $CuO.SO_3$ is in the pure color.

[60] See ante.

TABLE XI

Colors of Bordeaux mixtures 1:0.2 and 1:1

BORDEAUX MIXTURE 1:0.2	COMPOSITION OF TONE			BORDEAUX MIXTURE 1:1	COMPOSITION OF TONE		
	Color	White	Color		Color	White	Color
1% cupric sulphate.....	cendre blue	9.5	90.5	1% cupric sulphate.....	light methyl blue	9.5	90.5
2% cupric sulphate.....	cendre blue	9.5	90.5	2% cupric sulphate.....	light methyl blue	9.5	90.5

When Bordeaux mixtures (1:1) containing less than 1% cupric sulphate are made the basic sulphate or mixture of basic sulphates initially formed will depend on the dilution of the milk of lime, and to some extent on the size of the particles of hydrated lime in suspension, but the effect of the temperature of the solutions at the time of the reaction, at least between 10° to 30° C., is too inconsiderable to be considered.[61] The dilution of the milk of lime is the only factor of any importance as will appear from the following table.

TABLE XII

Basic sulphates initially formed in weak Bordeaux mixtures (1:1) when the milk of lime is more or less dilute

STRENGTH OF MIXTURE IN CUPRIC SULPHATE	DILUTION OF		PER CENT CaO IN SOLUTION	BASIC SULPHATES FORMED SUPPOSING THE SURFACES OF THE UNDISSOLVED CALCIC HYDRATE PARTICLES WITHOUT ACTION
	Cupric sulphate	Calcic hydrate		
per cent	*cc.*	*cc.*	*gram*	
0.5	15	85	0.127	$10\ CuO.SO_3 \frac{CuSO_4, 5H_2O}{CaO} = 5:1$
0.25	15	85	0.127	Mixture $\frac{CuSO_4, 5H_2O}{CaO} = 2\frac{1}{2}:1$
0.125	15	85	0.127	Mixture $\frac{CuSO_4, 5H_2O}{CaO} = 20:17$
0.5	50	50	0.127	Mixture $\frac{CuSO_4, 5H_2O}{CaO} = 25:3$
0.25	50	50	0.127	Mixture $\frac{CuSO_4, 5H_2O}{CaO} = 4:1$
0.125	50	50	0.127	Mixture $\frac{CuSO_4, 5H_2O}{CaO} = 500:63$

[61] The solubility of calcic oxide decreases as the temperature rises, but owing to the low solubility of the salt, the change is so small as to be negligible, water dissolving 0.127% at 10°C. and 0.126% at 30°C.

The above table shows that in Bordeaux mixtures weak in cupric sulphate, and in which the milk of lime is used very dilute, that, with the exception of the 0.5% mixture, the precipitates formed are mixtures of basic sulphates that are heavy and settle rapidly, whereas, if the milk of lime is used moderately strong, owing to the fact that the undissolved calcic hydrate particles take part in the reaction, the more voluminous basic sulphates tend to form. The differences between the rate of settlement of Bordeaux mixtures 1:1, prepared with different strengths of milk of lime, also furnishes evidence in support of the view that the method of preparation has no inconsiderable influence on the nature of the basic sulphate, or mixture of basic sulphates formed as will be seen from the data presented in the following table.

TABLE XIII

Relative settlement of weak Bordeaux mixtures 1:1 prepared with weak milk of lime and strong milk of lime

CUPRIC SULPHATE IN BORDEAUX MIXTURE	WEAK COPPER TO STRONG LIME				STRONG COPPER TO WEAK LIME			
	Settlement in relative numbers after				Settlement in relative numbers after			
	¼ hr.	½ hr.	1 hr.	2 hrs.	¼ hr.	½ hr.	1 hr.	2 hrs.
per cent								
0.5	100	200	412	1069	181	373	766	1393
0.25	403	969	1980	2493	969	1472	2048	2454
0.125	2078	2403	2584	2745	2272	2403	2563	2775

Effect of temperature of solutions on physical state of precipitate formed. While the temperature of the solutions has a certain influence on the character of the resulting precipitate in the case of Bordeaux mixtures prepared with lime water, the change produced is slight and much less important than in the case of Bordeaux mixtures prepared with milk of lime. In both cases, however, the change produced is different only in degree; with a rise of temperature the precipitates become more flocculent and less gelatinous.

Kelhofer[62] has shown that Bordeaux mixtures prepared at a high temperature settle more rapidly than mixtures prepared at ordinary temperatures.

The effect of temperature on Bordeaux mixtures prepared from milk of lime shows, however, unmistakably much sooner than is indicated by Kelhofer. Between 10°C. and 30°C. the character of the precipitate formed changes much more markedly than simple ocular inspection would lead one

[62] Kelhofer, W. Über einge Gesichtspunkte bei der Herstellung der Bordeauxbrühe. Internationaler phytophathologischer Dienst **1**. 1908.

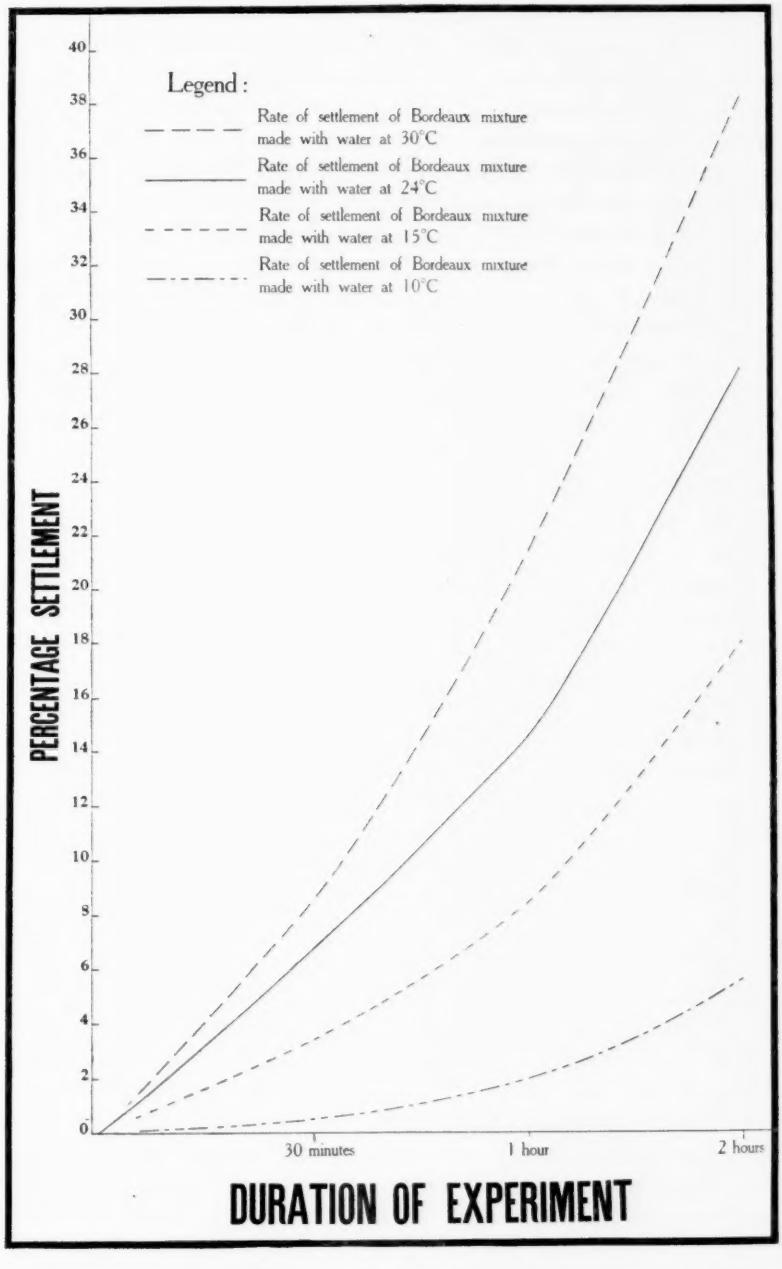

FIG. 2. Relative rate of settlement of 1% Bordeaux mixtures 1:1 made with water at different temperatures.

to expect. The mixtures prepared with water at 10°C. are much more gelatinous than those prepared with water at 30°C. The copper precipitate is more uniform in the mixture made at 10°C. than in that prepared at 30°C. in which it is somewhat denser and shows evidence of granulation (pl. 8, figs. 1 and 2).

If one compares the relative settlement of Bordeaux mixtures prepared in a similar manner he will find that the rate of settlement increases rapidly with a rise in temperature. In the case of 1% Bordeaux mixture (1:1), which is probably the most used at the present day, I obtained the results shown in the following figure. It should be noted that the temperatures given refer to the initial temperatures of the mixtures which were allowed to stand at room temperature. Somewhat more striking results would probably have been obtained had the mixtures been kept at their respective initial temperatures.

Effect of method of mixing on voluminousness of precipitate formed. The value of Bordeaux mixture as a wash depends largely on the density and volume of the precipitate formed by the interactions of the cupric sulphate and calcic hydrate. We have already seen that 10 $CuO.SO_3$ and 10 $CuO.SO_3$, 3 CaO are the least dense and most voluminous basic sulphates that can be formed. Were there no other factors, therefore, to be taken into consideration in the preparation of Bordeaux mixture, but that of precipitating the copper in as bulky a form as possible, we would only have to prepare the wash in such a manner as to produce 10 $CuO.SO_3$ or 10 $CuO.SO_3$, 3 CaO; but, owing to the fact that calcic oxide is only soluble to the extent of 0.12%, there would be some practical difficulties to be overcome in preparing these salts, though this can readily be accomplished as we shall see.[63] As, however, Bordeaux mixtures made with lime water are not much used in practice, and are not likely to be much used for various reasons that need not be considered here, it will be necessary for us to study only the effect of the method of mixing on the voluminousness of the precipitate formed in the case of Bordeaux mixtures prepared with milk of lime, 1% Bordeaux mixture (1:1) particularly.

From what we know regarding the behavior of particles in suspension, we would not expect Bordeaux mixtures (1:1) containing different amounts of cupric sulphate to settle equally rapidly, for, as is well known, the power of a precipitate to remain in suspension depends on the relative number, density, and volume of its particles. We would, therefore, expect that the rate of settlement of Bordeaux mixtures (1:1) would be approximately proportional to the per cent cupric sulphate taken. This, however, is by no

[63] Woburn Bordeaux mixture, for instance, is manufactured and sold as a proprietary compound.

means the case, the rate of settlement being enormously greater at weak concentrations than at high concentrations. These differences in rate of settlement are due in part to the fact that the solubility of the calcic hydrate increases rapidly as the concentration decreases; and this increase in the amount of soluble calcic hydrate causes the formation of higher basic sulphates or mixtures of basic sulphates which give heavier and less gelatinous precipitates. Rapidly settling mixtures begin to form, it will be remembered, as soon as the ratio cupric sulphate to calcic oxide becomes less than 3.75:1. One can not, therefore, draw conclusions from the behavior of a given Bordeaux mixture (1:1) regarding the behaviors of other stronger or weaker similar mixtures, though we can say that the stronger and weaker mixtures both form precipitates that are less gelatinous than 1% Bordeaux mixtures (1:1). It should however be noted that the various methods of preparing 1% Bordeaux mixture (1:1) do give approximately the same results with 1:1 mixtures of both lesser and higher strength in cupric sulphate. For instance in the case of 2% Bordeaux mixture (1:1) the average rate of settlement for the wash prepared by adding strong copper to weak lime is 1.3 times greater than for the wash prepared by adding weak lime to strong copper; in the case of 1% mixtures (1:1) the rate of settlement is 2.52 times greater, and in the case of ½% mixtures (1:1) 1.85 times greater.

The rate of settlement of 1% Bordeaux mixture (1:1) varies with the method of preparation, and there are nine different ways in which the mixture may be conveniently prepared in practice. These methods of preparation, which I will call, for convenience, method 1, and method 2, method 3, etc., are briefly described in the following table.

TABLE XIV

Description of methods used by the author in preparing 1% Bordeaux mixtures (1:1) for relative settlement studies

METHOD 1	METHOD 2	METHOD 3	METHOD 4	METHOD 5
Strong lime to strong copper	Strong lime to weak copper	Weak lime to strong copper	Lime to copper equal strengths	Lime and copper equal strengths poured together

METHOD 6	METHOD 7	METHOD 8	METHOD 9
Copper to lime equal strengths	Weak copper to strong lime	Strong copper to weak lime	Strong copper to strong lime

In *method 1* the requisite amount of a stock solution of cupric sulphate was taken and water added to 30cc.; the calcic oxide was freshly slacked

and the milk of lime diluted to 30 cc.; the milk of lime was then poured into the cupric sulphate solution, and water added to 100 cc. In *method 2* the stock solution of cupric sulphate was diluted to 85 cc., the freshly slacked lime to 15 cc.; the milk of lime was then poured into the cupric sulphate solution. In *method 3* the cupric sulphate solution was made up to 15 cc., and the milk of lime to 85 cc. The milk of lime was then poured into the solution of copper sulphate. In *method 4* the stock solution of cupric sulphate and the milk of lime were both diluted to 50 cc.; the milk of lime was then poured into the cupric sulphate. In *method 5* the reagents were diluted as in method 4 and were simultaneously poured into a third vessel.[64] *Method 6* is the converse of method 4. *Method 7* is the converse of method 3. *Method 8* is the converse of method 2. *Method 9* is the converse of method 1. As soon as poured together the solutions were thoroughly mixed by shaking for fifteen seconds.

In consulting the literature I have found that of the nine methods given above, six are recommended by one or another of the authors consulted, the same author not always being consistent. In a few instances (10 per cent) of the authors consulted I find that two or three methods of preparation are equally recommended, either 5 and 6, or 4 and 5, or 4, 5 and 6. The recommendations are, however, only in one instance based on an examination of the rate of settlement of the precipitate formed when Bordeaux mixture is made according to the above schemes, and in this instance even, method 5 was not examined, despite the fact that it is the most highly and most generally recommended, 41 per cent of the authors consulted having unqualifiedly recommended it, or mentioned it solely. For the method of making Bordeaux mixture so consistently advocated in the literature, i.e., method 5, there seems to be little or no experimental foundation. An examination of the literature in which experimental data is given shows this very clearly.

In 1895 Jones[65] using a 1.875% Bordeaux mixture (3:2) obtained the relative settlement shown in the following table.

TABLE XV

Relative settlement of 1.875% Bordeaux mixture (3:2) prepared in different ways. Method of preparation and settlement at the end of one hour

METHOD 1	METHOD 2	METHOD 4	METHOD 5	METHOD 6	METHOD 8
52%	15%	4%	13%	4%	13%

[64] This is the method usually recommended in the texts, the so-called standard method.

[65] Jones, L. R. Report of the botanist, Vermont Agr. Expt. Sta. Report **9**: 88. 1895.

This author with some disregard for the lesson taught by the above experiments concluded that Bordeaux mixture can be prepared equally well by methods 4, 5 and 6, and gives no reason for rejecting method 8 which the data shows equal to method 5. Jones was strongly of the opinion that in preparing Bordeaux mixture there should be no free copper present in the solution, at any time, and that thorough and long continued stirring was very beneficial. Bordeaux mixture prepared by adding the cupric sulphate and milk of lime simultaneously, stirring constantly the while settled one-half as rapidly as a mixture similarly prepared, but with less thorough stirring, and 9% less rapidly than a mixture not stirred at all, while the reagents were being brought together. In preparing Bordeaux mixture in which the lime used was just sufficient to precipitate all the copper, as determined by the potassium ferrocyanide test, there was an enormous difference between the mixtures prepared by adding the milk of lime tentatively, or in the necessary amount all at once. In the former case, the settlement of the precipitate was 50% of the original volume after 30 minutes; in the latter, 4% after one hour. Jones also found that Bordeaux mixtures settle with increasing rapidity with age.

In 1906 Warren and Voorhees[66] studied the relative rate of settlement of Bordeaux mixture. They used a 1% Bordeaux mixture (1:1) which they prepared according to methods 1, 2, 5 and 8, and found that method 2, strong lime to weak copper gave, the bulkiest precipitate. Their results are summarized in the following table.

TABLE XVI

Relative rate (in per cent) of settlement of 1% Bordeaux mixture (1:1) prepared in various ways. Results after standing thirty minutes, one hour and six hours

	METHOD 1[67]			METHOD 2			METHOD 5			METHOD 8		
Time, hours.	½	1	6	½	1	6	½	1	6	½	1	6
Settlement, %	50	77.27	86.36	1.13	20.45	50	9.09	31.81	63.63	4.54	31.81	68.18

The authors also studied the effect on the rate of settlement of adding the strong milk of lime to solutions of the cupric sulphate more and more dilute, and found, as the following table shows, that the more dilute the latter, the slower the rate of settlement of the precipitate.

[66] Warren, G. F. and Voorhees, J. A. Methods of making Bordeaux mixture. New Jersey Agr. Exp. Sta. Rep. **27:** 231. 1906.

[67] The text is not clear, either method 1 or method 9 may have been used.

TABLE XVII

Relative rate of settlement of 1% Bordeaux mixture (1:1) when strong milk of lime is added to various concentrations of the cupric sulphate

CONCENTRATION OF CUPRIC SULPHATE SOLUTION	SETTLEMENT OF PRECIPITATE AFTER		METHOD USED PREPARING MIXTURES
	45 minutes	4½ hours	
	per cent	*per cent*	
1 gm. $CuSO_4$ 5 H_2O in 25cc	36.36	56.81	1
1 gm. $CuSO_4$ 5 H_2O in 50cc	13.65	50.00	
1 gm. $CuSO_4$ 5 H_2O in 75cc	11.36	36.36	
1 gm. $CuSO_4$ 5 H_2O in 100cc[68]	1.90	34.09	2

The Duke of Bedford and Pickering[69] have studied the settlement of Bordeaux mixture prepared in different ways, and the result of their investigations is shown in the following table.

TABLE XVIII

Relative rate of settlement (in per cent) of 0.8% Bordeaux mixture prepared in various ways

	METHOD 1			METHOD 2			METHOD 4			METHOD 6			METHOD 8			METHOD 9		
Time, hours	½	1	2	½	1	2	½	1	2	½	1	2	½	1	2	½	1	2
Settlement, %	55	73	78	13	46	57	3	31	46	2	7	36	1	2	10	48	70	75

The results obtained, to quote the authors,[70] "appear at first sight to be hopelessly erratic, but, as a matter of fact, every feature exhibited by them is in strict accordance with what has been established as to the chemistry of Bordeaux mixture. The lime actually dissolved in the water is insufficient to react with the whole of the copper to form the basic sulphate of which freshly prepared Bordeaux mixture consists, hence some of the copper sulphate will react with the solid, dissolving particles of lime in the liquid, these becoming coated with a covering of basic sulphate; such particles will, of course, be much grosser and more dense than those of basic sulphate precipitated by dissolved lime, and the more they predominate the more quickly will the mixture of solids settle in the liquid. The more dilute the lime is to start with, the larger will be the proportion of basic sulphate formed by the lime water, and the smaller the proportion

[68] The Bordeaux mixture prepared in this case could not have been a 1% mixture, and therefore not strictly comparable with the others. In describing this experiment the authors state: "The copper sulphate was diluted with 0.25, 0.5, 0.75 and all the water before adding the concentrated lime and the remainder of the water." Loc. cit, p. 234.

[69] Loc. cit., ante.

[70] Loc. cit., p. 54 et seq.

formed on the particles of solid lime . . . . therefore, the results obtained by adding the copper to the lime must always be better than those obtained by adding the lime to the copper, comparing cases of similar dilution, for when the copper is added to the lime, the lime will at first be in excess . . . . and the basic sulphate will be formed from the dissolved lime, rather than from the solid particles, whereas during the addition of lime to copper sulphate, it will be the latter which is in excess during the addition and, not finding enough dissolved lime to combine with it, it will attack the solid particles, so that a larger proportion of dense precipitate will be formed." . . . . The dense precipitate formed "when both substances are mixed in a concentrated form, results, of course, from the fact that the greater part of the basic sulphate must be formed on the particles of solid lime, but, when the comparison is made after a certain lapse of time, it is found to be much more bulky than the other precipitates," and for the following reason: "The blue basic precipitate first formed is changed after a time to the violet sulphate, which is very compact, and that change occurs all the more rapidly, more easily the excess of lime present can be dissolved in the water, and so be in a position to bring about the chemical change. When most of the particles of lime are coated with basic sulphate, they will not be dissolved readily, and the final change will be delayed."

In 1911 Rogers[71] concluded from his experiments on settlement of Bordeaux mixture which were limited to a comparison of methods 2, 5 and 8 that the precipitate remaining longest in suspension was obtained when the cupric sulphate and calcic hydrate were prepared in equally dilute solutions and simultaneously poured together. The author used a 1.25% Bordeaux mixture (1:1.2). It should also be noted that method 2 gave a precipitate that settled more slowly than method 8.

Hawkins[72] studied the rate of settlement of 1% Bordeaux (1:0.75)[73] which he prepared in six different ways, as follows: 1° solutions equally diluted and poured simultaneously into a third vessel; 2° solutions equally diluted and the milk of lime poured into the copper sulphate; 3° the converse of 2 above; 4° strong lime to weak copper (5:95); 5° strong copper to weak lime (5:95); 6° strong lime to strong copper (5:5) which, barring, in some instances, slight differences in concentration, may be briefly described in the nomenclature I have used as methods 5, 4, 6, 8, 2 and 1. Methods 5, 4, 6,

[71] Rogers, S. T. The late blight of celery. Cal. Agr. Exp. Sta. Bull. 208. 1911.

[72] Hawkins, L. A. Some factors influencing the efficiency of Bordeaux mixture. U. S. Dept. Agr. Bur. Pl. Ind. Bull. 265. 1912.

[73] From the description of the *modus operandi* of the experiments, it would appear as if in some cases the author used 0.5% Bordeaux mixtures (1: 0.75), though in the data presented there is no evidence to this effect.

2, and 8 all gave equally voluminous and slowly settling precipitates when "properly mixed;" whereas method 1 produced a wash that settled rapidly. Hawkins also studied the effect of the duration of stirring on the rapidity of settlement of 1% Bordeaux mixtures (1:0.75) prepared according to methods 2 and 8, and obtained the results given in the following table.

TABLE XIX

Effect of duration of stirring on rate of settlement of 1% Bordeaux mixtures (1:0.75)

METHOD OF PREPARATION	SETTLEMENT IN RELATIVE NUMBERS AT END OF ONE HOUR			
	Times mixture was shaken			
	5	15	25	35
Method 5 (witness)	91.67 100.0			
Method 2	990.0	546.6	280	333
Method 8	650.0	100.0	100	100

A review of the literature leads one inevitably to the conclusion that further study on the physical properties of Bordeaux mixtures is not only desirable but necessary. Both the effect of the duration of stirring, as well as that of delayed stirring of the mixture may be profitably reinvestigated, and the lack of agreement between authors regarding the settlement of mixtures prepared in various ways leaves this subject still open to further experimentation.

Settlement of Bordeaux mixture. In our review of the literature we found that those authors who have studied the relative settlement of Bordeaux mixture prepared in different ways are far from being in agreement. This is due not as might at first be supposed to the fact that they used mixtures of various strengths, both in copper sulphate and ratios copper sulphate to lime, but rather to the fact that they did not study a sufficient number of methods of preparation. I have already pointed out that Bordeaux mixture may be conveniently made, not only in the laboratory but in practice as well, according to one or another of nine different methods though, as we have seen, no student of Bordeaux mixture has studied critically more than six of these methods. When, however, all of the nine methods are subjected to investigation, as I have done, using 1% Bordeaux mixtures (1:1) and averaging the results of eight experiments, the following results are obtained.

TABLE XX

Relative rate of settlement (in per cent) of 1% Bordeaux mixtures (1:1) prepared in different ways

	METHOD 1			METHOD 2			METHOD 3		
Time, hours	½	1	2	½	1	2	½	1	2
Settlement, %	12.12	23.44	45.07	3.64	7.40	14.72	4.38	8.83	17.07
	METHOD 4			METHOD 5			METHOD 6		
Time, hours	½	1	2	½	1	2	½	1	2
Settlement, %	3.21	6.14	11.34	4.10	8.00	15.35	3.65	7.34	13.69
	METHOD 7			METHOD 8			METHOD 9		
Time, hours	½	1	2	½	1	2	½	1	2
Settlement, %	2.49	5.18	10.5	5.45	11.52	29.1	13.86	27.27	52.75

Now if we consider the results obtained by previous workers in the light of the above data, as I have done in the following table, it will at once be apparent that the differences between authors is, with one notable exception, more apparent than real. For instance, method 1 gave a more rapidly settling Bordeaux mixture than the standard of comparison (method 8) in all cases. Jones and I have found that method 6 gives mixtures settling more slowly than either the standard of comparison, or method 5. In the case of method 5, it will be observed that the rate of settlement is either equal to or less than that of method 8. Again, in the case of method 4, Jones and I have both obtained mixtures settling more slowly than those prepared by methods 5 and 8; the data for method 2

TABLE XXI

Tabular resumé of the work of various authors on rate of settlement of Bordeaux mixtures.

REFERENCE NO.	AUTHOR	SETTLEMENT (IN RELATIVE NUMBERS) AFTER ONE HOUR								
		Method 1	Method 2	Method 3	Method 4	Method 5	Method 6	Method 7	Method 8	Method 9
A	Warren and Voorhees	242	64			100			100	
B	Jones	400	115		30	100	30		100	
C	Rogers		164			64			100	
D	Duke of Bedford and Pickering	3650	2300		1550		350		100	3500
E	Hawkins		100		100	100	100		100	
F	The writer	169	61	74	52	64	60	49	100	195

on the other hand is conflicting. The data given by the Duke of Bedford and Pickering shows an increasing rate of settlement as one proceeds from method 8 to method 1, results which are not in harmony with the data of the other sources quoted, or my own.

It being clear that the results I have obtained are not materially in conflict with those of previous investigators, the Duke of Bedford and Pickering's data in part excepted, we may proceed to study the data summarized in table XX more at length.

In studying the relative settlement of Bordeaux mixture (1:1) prepared according to the methods indicated, we will first notice that, within experimental error, the rate of settlement of the mixtures, no matter how prepared, is directly proportional to the time. This fact is more clearly brought out in the graph (pl. 9) than in the table, a mere inspection of the graph leading one immediately to the conclusion that during the time interval of the experiment no physical or chemical changes of any moment occur in the mixtures.

Another fact more strikingly brought out in the graph than in the table is that method 5, the method of preparation universally recommended, is not the method that gives the most slowly settling mixture; that, in fact, methods 7, 4, 6 and 2 are superior to it.

It will be remembered that according to the theoretical views advanced by the Duke of Bedford and Pickering[74] those mixtures in which the copper is added to the lime should give more slowly settling mixtures than those obtained by adding the lime to the copper. The data I have obtained, however, do not support this conclusion.

I obtained the most slowly settling mixture by adding weak copper to strong lime, the next best by adding lime to copper equal strengths, the third best by adding copper to lime equal strengths, the 4th best by adding strong lime to weak copper, while method 8, strong copper to weak lime which gave such good results with the Duke of Bedford and Pickering only occupies seventh place with me. The results I have obtained are, however, in no sense accidental as the detail for all the experiments given in the following table will show. I omit methods 1 and 9 as every one is agreed that they yield unsatisfactory washes.

As will be seen from the table, Bordeaux mixture prepared according to method 8 never settled less rapidly than mixtures prepared according to methods 7, 5, 4 and 2, and only once more rapidly than method 6, and but twice more rapidly than mixtures prepared by method 3. It is therefore clear that the explanation advanced by the Duke of Bedford and Pickering will not hold for 1% Bordeaux mixture (1:1).

[74] See ante.

TABLE XXII

Relative settlement of 1% Bordeaux mixtures (1:1) prepared in different ways
Method of preparation. Settlement (in relative numbers) after two hours

Method 8	Method 7	Method 6	Method 5	Method 4	Method 3	Method 2
120	81	83	100	83	95	90
108	70	110	100	90	115	100
140	75	60	100	60	120	100
145	75	82	100	70	84	75
127	70	100	100	66	116	100
150	37	133	100	77	115	75
146	125	80	100	80	114	125
192	50	114	100	85	208	120
241			100		104	
108			100			
150			100			

Let us see, however, inconsistent as it would at first seem to be, whether or not the behavior of the mixtures may be accounted for in some other way. A careful perusal of the data discloses the fact that the rate of settlement of 1% Bordeaux mixtures 1:1 increases with the amount of soluble calcic hydrate present at the time of their preparation. If we assume that at ordinary temperatures water dissolves 0.12% calcic oxide, though from our present point of view the absolute amount is immaterial, we would find the relation between method of mixing, rate of settlement, and per cent calcic oxide in solution to be as follows:

TABLE XXIII

Relation between method of mixing, rate of settlement and per cent calcic oxide in solution

METHOD OF MIXING	SETTLEMENT AT END OF ONE HOUR IN RELATIVE NUMBERS	CaO IN SOLUTION
		per cent
Weak copper to strong lime (method 7)	100	0.018
Lime to copper equal strengths (method 4)	106	0.060
Copper to lime equal strengths (method 6)	114	0.060
Strong lime to weak copper (method 2)	124	0.018
Lime and copper equal strengths poured together simultaneously (method 5)	130	0.060
Weak lime to strong copper (method 3)	150	0.096
Strong copper to weak lime (method 8)	203	0.096

A perusal of the above table shows that pouring weak copper into strong lime, or strong lime into weak copper gives a more slowly settling precipitate than when weak lime is poured into strong copper or strong copper

into weak lime. Now the only difference between these two sets of methods of preparation is that, when the reagents are brought together in the former, the amount of calcic oxide in solution is one-fifth that present in the latter. In the case of methods 7 and 2, lower basic sulphates form than in the case of methods 3 and 8.

The table also clearly shows that, when the lime and copper are equally diluted and mixed according to methods 6, 4 or 5, the mixtures obtained settle more slowly than those prepared by adding weak lime to strong copper (method 3) or strong copper to weak lime (method 8), and more rapidly than the mixtures prepared by adding weak copper to strong lime which is in agreement with the view I am upholding. Mixtures prepared by adding strong lime to weak copper fall, however, somewhat out of their proper place and settle more rapidly than mixtures prepared by methods 7, 4 and 6, but more slowly than those prepared by methods 5, 3 and 8.

A further point worthy of note is that the 1% mixtures behave in a similar but less striking manner to 1:1 mixtures weak in cupric sulphate. It has been explained earlier that 0.5% mixtures and 0.25% mixtures, made by adding weak copper to strong lime, settled during the first hour unmistakably less rapidly than mixtures of the same respective strengths made by adding strong copper to weak lime.

The conclusion seems warranted, therefore, that the amount of soluble calcic hydrate present when Bordeaux mixture is made directly affects the nature of the basic sulphate or basic sulphates formed, and that to its greater or lesser preponderance the divers effects of the methods of mixing are largely due.

So far we have studied the rate of settlement of 1% Bordeaux mixture (1:1). We may now ask (a) what effect reducing or increasing the per cent copper without changing the ratio copper sulphate to lime has on the rate of settlement, and (b) what effect, for a given percentage of copper, changing the ratio copper sulphate to lime has on the relative rate of settlement of the mixtures.

a. To the first question we may answer that when the copper sulphate is used at a higher concentration than 1% the mixtures formed settle more slowly, and when used at a lesser concentration more rapidly. This is, of course, exactly what one would expect were the mixtures formed physically and chemically identical with the 1% mixture. We would expect a 2% Bordeaux mixture (1:1) to settle approximately one-half as rapidly as a 1% mixture (1:1), and a 0.5% mixture (1:1) to settle twice as rapidly as a 1% mixture (1:1). In practice, however, these results are very far from being attained. As will be seen from the following table, 2% and 4% Bordeaux mixtures (1:1) owing probably to lack of fluidity, settle

quite slowly. Bordeaux mixtures containing less than 1% cupric sulphate, on the other hand, settle proportionally much more rapidly than one would expect, owing, at least in part, to the formation of higher and denser basic sulphates, or mixtures of basic sulphates.

TABLE XXIV

Relative settlement of Bordeaux mixtures (1:1) containing different percentages of cupric sulphate. Method of mixing: Strong copper to weak lime (method 8)

MIXTURE USED		SETTLEMENT (IN RELATIVE NUMBERS) AFTER		
		½ hour	1 hour	2 hours
4.0%	(1:1)	16	30	65
2.0%	(1:1)	25	50	103
1.0%	(1:1)	100	265	515
0.5%	(1:1)	460	785	1210
0.25%	(1:1)	1310	1550	1700
0.125%	(1:1)	1712	1785	1864

b. The Duke of Bedford and Pickering[75] have expressed the view that Woburn Bordeaux mixture, a mixture in which the ratio cupric sulphate to calcic oxide is 1:0.2 settles more slowly than mixtures prepared with greater or lesser amounts of lime. This view is readily confirmed as the data collected in the following table shows.

TABLE XXV

Settlement in relative numbers of Bordeaux mixtures prepared with different ratios cupric sulphate to calcic oxide

2% (1:1)			2% (1:0.5)			2% (1:0.25)			2% (1:0.2)		
½hr.	1hr.	2hrs.	½hr.	2hrs.	2hrs.	½hr.	1hr.	2hrs.	½hr.	1hr.	2hrs.
100	193	364	28	64	185	28	71	193	2	3	6
1% (1:1)			1% (1:0.5)			1% (1:0.25)			1% (1:0.5)		
½hr.	1hr.	2hrs.	½hr.	1hr.	2hrs.	½hr.	1hr.	2hrs.	½hr.	1hr.	2hrs.
100	205	455	72	150	355	55	122	294	5	10	20
½% (1:1)			½%)1:0.5)			½% (1:0.25)			½% (1:0.2)		
½hr.	1hr.	2hrs.	½hr.	1hr.	2hrs.	½hr.	1hr.	2hrs.	½hr.	1hr.	2hrs.
100	164	212	60	109	183	23	56	89	24	49	79

[75] Loc. cit.

A perusal of table XXV not only clearly shows that Woburn Bordeaux mixture settles more slowly than mixtures in which the ratio cupric sulphate to calcic oxide is less than 5:1, but also that the rate of settlement of the mixtures increases as the ratio cupric sulphate to calcic oxide approaches 1:1. This increased rate of settlement is due to a decrease in the amount of 10 $CuO.SO_3$ formed as may be gathered from the fact that the mixtures used in the table give the following results on boiling:

$\frac{1}{2}\%$ $(1:\frac{1}{4})$ very slight formation of cupric oxide
2% $(1:1)$; 1% $(1:1)$ } slight formation of cupric oxide
2% $(1:\frac{1}{2})$; 1% $(1:\frac{1}{2})$ }
2% $(1:\frac{1}{4})$; 1% $(1:\frac{1}{4})$ formation of cupric oxide more abundant
$\frac{1}{2}\%$ $(1:1)$; $\frac{1}{2}\%$ $(1:\frac{1}{2})$ no cupric oxide formed

Effect of impurities on rate of settlement. As ferrous sulphate is a common impurity of copper sulphate, and quicklimes may contain besides calcic carbonate, magnesic carbonate, or magnesic oxide, or mixtures of both salts, I thought it would be of some interest to determine what individual action these several salts had on the rate of settlement of 1% Bordeaux mixture (1:1) and the more especially since, as has been seen earlier, they are of unequal value in retarding crystallization. Should the salts that most retard crystallization also decrease the rate of settlement of Bordeaux mixtures, a knowledge of this fact would have some practical importance. The practitioner would know if he had to choose one or the other of two impure quick limes, for instance, which one was to be preferred, and why.

As we shall see, however, the several salts behave more nearly alike as regards effect on rate of settlement than they do in the matter of delaying crystallization, though my experiments show that those salts that are most efficient for the latter purpose are also more effective in retarding rate of settlement. For instance, magnesic carbonate, which delays crystallization most markedly, is also most active in retarding settlement, as will be seen from the accompanying figure. Magnesic oxide being next best, while calcic carbonate and ferrous sulphate, which have little or no value in preventing crystallization, follow in the order named. When one considers, however, the effect on rate of settlement of each of the above salts with respect to their action when used at the strengths of 5%, 10% and 15% considered individually rather than as a collective average, the results obtained are not as well marked as will be seen from the following table.

Taking into consideration the effect of the magnesic salts, calcic carbonate and ferrous sulphate both in retarding rate of settlement and delaying crystallization, the conclusion may safely be drawn that magnesian quicklimes that slake well can be used, even advantageously, in preparing Bordeaux mixtures.

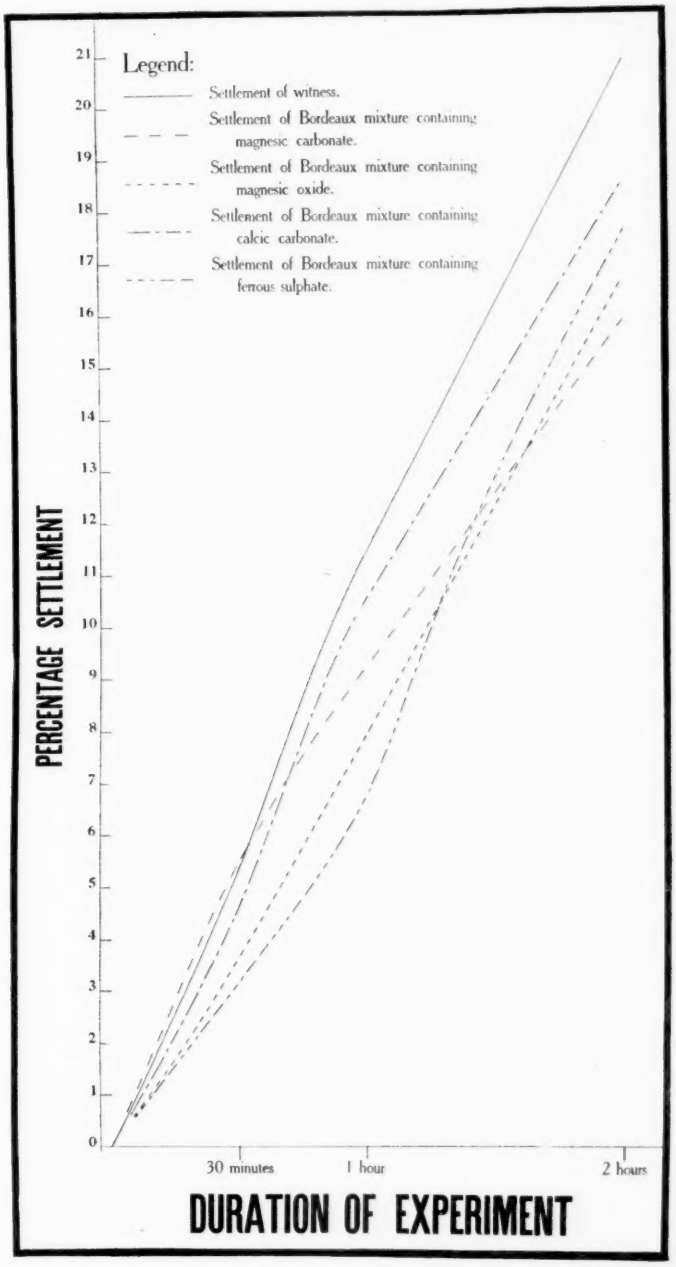

FIG. 3. Effect of impurities on rate of settlement of 1% Bordeaux mixture (1:1). The data from which the several curves were plotted represent the averages of all the experiments performed with each individual salt.

TABLE XXVI

Effect of impurities on the rate of settlement (in relative numbers) of 1% Bordeaux mixture (1:1)

		PER CENT	½ HR.	1 HR.	2 HRS.	PER CENT	½ HR.	1 HR.	2 HRS.	PER CENT	½ HR.	1 HR.	2 HRS.
	Witness		100	211	383								
Bordeaux mixture containing	Magnesic carbonate	5%	109	200	294	10%	109	157	297	15%	89	164	283
	Magnesic oxide	5%	85	200	345	10%	72	145	313	15%	46	105	259
	Calcic carbonate	5%	85	180	339	10%	101	192	351	15%	76	192	329
	Ferrous sulphate	5%	52	111	313	10%	52	114	310	15%	72	150	345

Effect of temperature on rate of settlement of Bordeaux mixture. The effect of the temperature of the copper sulphate solution and the milk of lime when Bordeaux mixture is made has a marked influence on the physical state of the mixture, as we have already seen, and is, therefore, deserving of some consideration in a chapter devoted to a consideration of the factors affecting the rate of settlement of Bordeaux mixtures.

The effect of temperature on the rate of settlement of Bordeaux mixture is very much more marked than one would expect. The amount of settlement of a 1% mixture 1:1 made with water at 30° C. is at the end of two hours more than six times that of a mixture made with water at 10° C.; a mixture made with water at 24°C. settles about five times as rapidly during the same length of time as a mixture made with water at 10°C.; a mixture prepared with water at 15°C. settles more than three times as rapidly as a mixture made with water at 10°C.

These facts are strikingly brought out in the following table, as well as in the graph on page 153.

TABLE XXVII

Effect of initial temperature of 1% Bordeaux mixture 1:1 on rate of settlement of the copper precipitate.

DURATION OF EXPERIMENT	SETTLEMENT IN RELATIVE NUMBERS			
	Initial temperature of mixture			
	10°C.	15°C.	24°C.	30°C.
½ hour	100	700	1360	1900
1 hour	400	1650	2900	4250
2 hours	1120	3600	5640	7640

I have pointed out in a previous chapter that when Bordeaux mixtures are prepared with water at moderate temperatures (20 to 30°C.) the precipitate formed is not as gelatinous as that obtained with water at

10 to 15°C. The studies on the rate of settlement of Bordeaux mixtures prepared at 10°C., 15°C., 24°C., and 30°C., the results of which are shown in the above table (see also graph page 153) clearly indicate that not only are the precipitates formed when Bordeaux mixtures are made with water above 20°C. much more granular than the precipitates obtained with cold water, but they are also much more dense. Now these facts are of very considerable importance to the practitioner to whose interest it is to produce in so far as possible the most highly gelatinous Bordeaux mixture, for the adhesiveness of the active precipitate is at least proportional to its degree of gelatinization; but further, the colder the water used in preparing the mixture the more slowly will it deteriorate. Hence, *ceteris paribus*, not only is a mixture prepared with cold water more adhesive when freshly made than a mixture prepared with tepid water, but also the rate at which its adhesiveness approaches zero, i.e., the point of complete deterioration, is much slower than in the case of the latter. Furthermore, in the case of Bordeaux mixture, the effectiveness is also proportional to the degree of adhesiveness,[76] whence the efficiency of the unit copper in the mixtures prepared with cold water is much greater than the efficiency of the unit copper in the washes prepared with tepid water.

Effect of delayed stirring. It is generally believed in practice, and Jones, as we have seen, offers some experimental evidence in favor of the view, that delayed stirring produces a more rapidly settling, that is a less gelatinous Bordeaux mixture than stirring begun the moment the copper sulphate and the milk of lime are brought together. This opinion, however, does not appear to be well founded. In studying the effect of delayed stirring on Bordeaux mixtures prepared according to methods 3, 5 and 7, I found in all these cases that there was no proportionality between the time elapsed before stirring and the rate of settlement, nor, what is even more important, were the results obtained for the methods of preparation studied concordant. Delayed stirring may, or may not be injurious.

The results of my experiments are shown graphically in plate 9, and the data for the individual experiments in the following table.

In the case of method 5 when the stirring was delayed for eight minutes the wash obtained settled 45.45% more rapidly at the end of one-half hour than the witness, but at the end of two hours the difference was much less marked, the rate of settlement of the former being only 13.20% greater than that of the latter; whereas in the case of the mixtures stirred after four and two minutes respectively the rate of settlement was throughout slower than for the wash stirred immediately. When the Bordeaux mixture was prepared according to method 3, on the other hand, I found

[76] This is not of course necessarily true of all the copper fungicides.

TABLE XXVIII

Effect of retardation of stirring on the settlement of 1% Bordeaux mixture (1:1). Settlement in relative numbers

STIRRED AFTER 8 MIN.			STIRRED AFTER 4 MIN.			STIRRED AFTER 2 MIN.			WITNESS. STIRRED IMMEDIATELY		
½ hr.	1 hr.	2 hrs.	½ hr.	1 hr.	2 hrs.	½ hr.	1 hr.	2 hrs.	½ hr.	1 hr.	2 hrs.
A. Mixtures prepared by adding weak copper to strong lime (Method 7)											
50	*100*	*300*	100	200	500	*50*	*100*	*400*	100	200	500
50	*125*	*240*	*25*	*75*	*200*	*50*	*125*	*250*	100	175	350
200	300	600	100	*100*	*400*	100	200	600	100	200	600
B. Mixtures prepared by adding weak lime to strong copper (Method 3)											
60	*120*	330	*90*	169	378	*50*	*120*	330	100	160	300
112	291	560	350	612	770	300	540	660	100	275	500
53	*95*	*196*	*64*	*185*	*307*	*53*	*121*	*248*	100	200	350
100	200	370	*85*	*170*	*340*	*86*	*171*	*310*	100	200	360
140	280	476	100	220	460	*80*	*180*	*360*	100	220	460
70	*126*	*336*	*85*	*153*	*323*	*71*	*142*	*298*	100	200	340
72	*128*	*252*	160	256	400	210	315	420	100	160	320
C. Mixtures prepared by pouring together simultaneously equally diluted copper sulphate and milk of lime (Method 5)											
100	*250*	550	100	300	650	100	*200*	600	100	300	530
400	748	1300	100	400	750	100	350	*700*	100	350	750
50	*175*	*275*	*75*	*150*	*300*	*50*	*125*	600	100	225	400
130	260	390	100	230	400	100	230	*330*	100	230	360

that delaying the stirring for eight minutes produced a wash that settled during the first half hour 27.24% more slowly than the witness, the difference at the end of two hours being still in favor of delayed stirring by 10.21%. The mixtures stirred after four minutes, and two minutes, however, settled more rapidly than the mixture stirred immediately. These results are the reverse of those obtained when the mixture is made according to method 5. In the case of method 7, I found that delayed stirring in all cases produced more slowly settling mixtures than the witness, though the mixture stirred after four minutes showed a slower rate of settlement than the mixtures stirred after two and eight minutes respectively.

A perusal of the table XXVIII also shows that in the case of method 3 stirring delayed for eight minutes produces mixtures, settling more rapidly than the witness at the end of one-half hour in three-sevenths of the experiments, and after the lapse of two hours in four-sevenths of the experiments; when the stirring was delayed for four minutes, or two minutes, the rate of settlement was respectively two-sevenths and three-sevenths.

In the case of method 5, stirring delayed for eight minutes produced more rapidly settling mixtures at the end of one-half hour and two hours in one-half of the experiments. When the stirring was delayed for four minutes, or two minutes, only one-fourth of the experiments showed a more rapid rate of settlement than the witness after one-half hour, though at the end of two hours, one-half of the experiments settled more rapidly.

In the case of method 7, delayed stirring for eight minutes gave mixtures settling more rapidly than the witness in one-third of the experiments at the end of one-half hour, but at the end of two hours the settlement was never greater than in the case of the mixtures stirred immediately. Stirring delayed for four minutes, or two minutes, never produced mixtures settling more rapidly than the witness.

The above facts warrant the conclusion that in practice no ill effects will result if Bordeaux mixture is thoroughly stirred only after the spray tank has been filled. Filling a spray tank requires a little time and whatever way the mixture is made there will be greater churning in the liquid than there is in a laboratory experiment in which the reagents are used in such small quantities that they mix rather poorly on being brought together. In practice, delayed stirring will have less effect on the rate of settlement of Bordeaux mixture than was obtained in the experiments above recorded.

Effect of degree of stirring on rate of settlement. Jones[77] considered that long-continued stirring had a very marked retarding influence on the rate of settlement of Bordeaux mixture; the Duke of Bedford and Pickering,[78] on the other hand, believed that a thorough mixing of the milk of lime and cupric sulphate solution was all that was necessary. Hawkins[79] has, however, given experimental data confirming the view of Jones, and I, in turn, have obtained the following results.

TABLE XXIX

Effect of thoroughness of stirring on rate of settlement (in relative numbers) of 1% Bordeaux mixture (1:1). Method of mixing: Weak copper to strong lime (Method 7)

	MIXTURE SHAKEN 3 SECS.			MIXTURE SHAKEN 7 SECS.			MIXTURE SHAKEN 15 SECS.		
Time, hours	½	1	2	½	1	2	½	1	2
Rate of settlement	120	319	669	120	360	852	100	240	660
	MIXTURE SHAKEN 30 SECS.			MIXTURE SHAKEN 60 SECS.			MIXTURE SHAKEN 120 SECS.		
Time, hours	½	1	2	½	1	2	½	1	2
Rate of settlement	120	300	679	100	260	620	100	180	500

[77] Loc. cit. [78] Loc. cit. [79] Loc. cit.

The above table does not confirm the view that stirring after a homogeneous mixture has been obtained produces a more slowly settling wash. No proportionality exists between time shaken and rate of settlement obtained, though some such relation should be evident were stirring *per se* a factor influencing rate of settlement. It should, however, be noted that long continued stirring, for instance, one hundred and twenty seconds, instead of fifteen seconds, the latter being what I might perhaps call the standard length of time of stirring used in the studies reported in this paper, gives mixtures that usually settle more slowly than those stirred for a shorter period of time, the difference in rate of settlement being more noticeable after the mixtures have settled two hours or somewhat longer. It is, however, problematical that this difference in rate of settlement is sufficient to warrant any emphasis being laid on long continued stirring, since Bordeaux mixture in a spray tank even not provided with an agitator, will be continually in motion, and initial differences due to the degree of stirring would become negligable even before the mixture was put in service.

V. TYPES OF BORDEAUX MIXTURES; THEIR PREPARATION AMD PROPERTIES

We have now to consider the preparation of Bordeaux mixtures. Lafon[80] evidently in error says that 0.335 gram calcic oxide is required to precipitate 1 gram of cupric sulphate, while Savastano[81] gives 0.225 gram as the amount required. This would satisfy the reaction were the copper precipitated in the form of the hydroxide, but, as it is now known that the copper occurs in the form of basic sulphates, one cannot properly speak of a given quantity of calcic hydrate satisfying the reaction without at the same time describing the basic salt that is to be formed.

As we have seen, the lowest basic sulphate that can be formed is obtained by precipitating 1 gram of cupric sulphate by 0.169 gram calcic oxide. It is, therefore, possible to prepare a Bordeaux mixture in which the ratio cupric sulphate to calcic oxide is as 6:1 but as the precipitate obtained is heavy and settles rapidly it can not be advantageously used in practice.[82] The basic sulphate formed, on the other hand, when the ratio cupric sulphate to calcic oxide is as 5:1 forms a floccoso-gelatinous precipitate which is quite permanent. This basic sulphate is generally known

[80] Lafon, R. Mode d'action des sels de cuivre dans le traitement des maladies cryptogamiques. Journ. Soc. Nat. Hort. France. Ser. 4, **8**: 356. 1907.

[81] Savastano, L. Loc. cit., p. 252. See also Woburn Experimental Fruit Farm Report **6**: 188.

[82] The small amount of soluble copper present in the mother liquor (0.0025%) is of no material importance.

as Woburn Bordeaux mixture, and may readily be prepared from stock solutions as follows:

A		B	
Quicklime	1[83] parts.	Copper sulphate	10 parts.
Water	to 100 parts.	Water	to 100 parts.

The mixture is then made by pouring 2.5 parts of B into 85 parts of A and making up to 100 parts with water.

As calcic oxide is only slightly soluble in water, 1:800, at ordinary temperatures, the mixture should be tested for the presence of soluble copper,[84] and if any is found lime water must be added until precipitation is complete. The Bordeaux mixture as above prepared contains 0.5% copper sulphate and can be made but very little stronger than this directly owing to the low solubility of calcic hydrate. If a stronger mixture is desired, it may, however, be readily prepared in the following manner:

A mixture is made as per the above formula, run into a storage tank and allowed to settle twenty-four hours. The supernatant clear liquid is then decanted. In the meanwhile another lot of the wash has been prepared and is added to the first as soon as decantation has been completed. After the precipitate has settled sufficiently, a volume of the supernatant liquid equal to that occupied by the first precipitate is withdrawn. One will then have a 1% mixture. By repeating the process once more a 2% mixture may be obtained.

Cavazza in 1886 advocated a Bordeaux mixture prepared with lime water which would be, according to the formula given by Lodeman,[85] a lower basic sulphate than Woburn Bordeaux mixture, and physically not so well adapted to fungicidal uses.

The Bordeaux mixtures made with milk of lime are much more generally used than those prepared with lime water. One of the reasons is, of course, that it is necessary to limit their strength to 0.5% when lime water is used, unless the roundabout method above described is resorted to; whereas in practice a mixture weaker than 1% cupric sulphate is advocated only in special cases, and stronger solutions, particularly in Europe, are still currently used. It may be said that the usual practice in preparing Bordeaux mixture, whatever the strength of copper sulphate used, and we have seen

[83] After dilution the milk of lime should be stirred at frequent intervals for an hour or so, and allowed to settle. As soon as clear the lime water may be drawn off as required.

[84] Potassium ferrocyanide is the reagent best suited for this purpose.

[85] If the formula for Cavazza's Bordeaux mixture given by Sostegni, loc. cit., ante, is correct, i.e., a mixture containing 0.6% cupric sulphate instead of 0.72%, then the basic sulphate obtained would resemble more closely 10 $CuO.SO_3$.

that this may vary between 0.5 and 3%, is to precipitate the copper by means of milk of lime. The amount of milk of lime used for this purpose varies, it will be remembered, between wide limits; the quicklime used for preparing the milk of lime, may be less than, equal to, or more than the weight of copper sulphate taken. The European authors have generally recommended the use of less quicklime than copper sulphate, whereas in the United States an equal weight of both salts is usually advocated. According to the amount of quicklime used per unit of copper sulphate, we may, therefore, have, to use the rather questionable nomenclature of the literature, acid, neutral, or basic Bordeaux mixtures. The neutral Bordeaux mixtures are usually prepared by adding milk of lime to the solution of copper sulphate until the mixture is alkaline to litmus or phenolphthalein.[86] Bourcart,[87] however, prepares the mixture with just enough milk of lime to produce a wash the filtrate of which gives no reaction with either blue litmus or tumeric paper. The acid Bordeaux mixtures are prepared by adding 0.1 to 0.2% copper sulphate to a neutral mixture, i.e., a mixture just alkaline to litmus or phenolphthalein, the smaller amount to 1% mixtures, the larger to 2% mixtures. The alkaline Bordeaux mixtures contain more milk of lime than is needed to produce alkalinity, the usual practice being, at least in the United States, to use equal weights of the salts. The formulae for the preparation of the three types of Bordeaux mixture recognized in the literature would, therefore, be as follows.[88]

1. Acid Bordeaux mixture. Prepare 100 parts of a 1% to 2% neutral Bordeaux mixture and add to it 0.1 to 0.2 parts copper sulphate previously dissolved in 10 parts water.

2. Neutral Bordeaux mixture; copper sulphate 1 part; milk of lime q. s. to alkalinity; water to 100 parts.

3. Basic Bordeaux mixture: copper sulphate 1 part; quicklime 0.5 to 1 part; water to 100 parts.

It will have been noticed that an acid Bordeaux mixture is made by adding a certain amount of copper sulphate to a neutral mixture. We would therefore expect an acid Bordeaux mixture to contain some of its copper in the form of a lower basic sulphate than is present in a neutral mixture. The reader will remember that the evidence is in favor of the view first advanced by Pickering that the copper in Bordeaux mix-

[86] Lafon B. Loc. cit. ante.
Savastano, L. Loc. cit., p. 254.

[87] Bourcart, E. Les maladies des plantes, p. 329. Paris, 1910.

[88] The solution of copper sulphate and the milk of lime should, in each case, be diluted and mixed as nearly as may be by the method producing the most slowly settling mixture. In the case of "acid" and "neutral" washes, method 2 is indicated.

ture containing 1% copper sulphate or thereabouts is precipitated as a mixture of the basic sulphate 10 $CuO.SO_3$ and 10 $CuO.SO_3$ 3 CaO. Now in the case of neutral Bordeaux mixtures it can be shown that the amount of 10 $CuO.SO_3$ present depends on the care with which they are prepared: if the mixtures are made just alkaline 10 $CuO.SO_3$ predominates; if the mixtures are quite alkaline 10 $CuO.SO_3$ and 10 $CuO.SO_3$, 3 CaO are formed, the latter probably predominating. Acid Bordeaux mixtures will, therefore, usually contain their copper in the form of 10 $CuO.SO_3$. Lower basic sulphates may be present, however, soluble copper being sometimes present in the filtrate; but, in practice, their presence must be exceptional as an alkaline reaction would hardly be observed under field conditions when less than 0.25 gram calcic oxide was used to precipitate 1 gram copper sulphate. Taking, however, the value of 0.25 gram, and assuming the formation of 10 $CuO.SO_3$, we would have 0.05 gram free calcic oxide in the mixture which would require for neutralization 0.25 gram cupric sulphate. But the formulae for the preparation of acid Bordeaux mixtures, as we have seen, do not call for more than 100 to 200 grams copper sulphate per hectolitre, i.e., 0.1 to 0.2%. Hence under ordinary conditions acid Bordeaux mixtures will be quite or nearly *neutral* and therefore composed largely of the basic sulphate 10 $CuO.SO_3$.

The alkaline Bordeaux mixtures do not possess peculiarities deserving especial mention. I may note, however, that such mixtures are not usually spoken of as alkaline when the ratio copper sulphate to quicklime is greater than 2:1.

Bordeaux mixtures are more readily prepared from stock solutions made up in the ratios in which they are to be used. The strength at which the stock solutions shall be made up depends, however, upon the solubility of the salts used (in the case of Bordeaux mixture only the copper sulphate need be considered), upon the size of the available storage vessels, and upon the amount of wash required. The current usage in the United States at least, is to use the copper sulphate at a strength of 10%, although a 20% solution can be equally readily prepared, but for reasons that are not apparent is less used in practice. In preparing the following stock solution formulae I have, however, used a 20% solution of copper sul-

For acid Bordeaux mixture

A. Copper sulphate.....20 parts
Water.....to 100 parts
B. Water.....to 100 parts
Quick lime, 90% pure....7 parts
C. Copper sulphate. 20% sol. 10 parts
Water.....to 100 parts

For neutral Bordeaux mixture

A. Copper sulphate.....20 parts
Water.....to 100 parts
B. Quick lime, 90% pure....7 parts
Water.....to 100 parts

phate, as stock solutions so prepared have economic advantages that justify their *raison d'être*.

The above formulae for the acid and neutral Bordeaux mixture stock solutions have been so prepared that aliquots of each should be taken in preparing the washes. It is, however, permissible when preparing acid Bordeaux mixture to use twice as much of stock solution C as of A and B.

For alkaline Bordeaux mixture

A. Copper sulphate.....20 parts
Water.....to 100 parts

B. Quick lime, 90% pure....10 to 20 parts
Water.....to 100 parts

In preparing the stock solutions of the copper sulphate and milk of lime, the custom is to allow for the increase in volume accompanying the dissolution of the copper sulphate and the hydration of the lime, the assumption being that unless this is done a perceptible error will be introduced. As the following table shows, however, the error produced by making up

TABLE XXX

Change in volume produced by dissolving copper sulphate and hydrating lime in a given amount of water

VOLUME OF WATER TAKEN	AMOUNT OF SALT ADDED	VOLUME OBTAINED	SALT IN FINAL VOLUME	ERROR
cc.		*cc.*	*per cent*	*per cent*
100	10 grams cupric sulphate	104	9.61	3.90
100	20 grams cupric sulphate	108	18.51	7.45
100	10 grams calcic oxide	104	9.61	3.90
100	20 grams calcic oxide	106	18.86	5.70

the stock solutions with x number of gallons rather than to x gallons is negligible in practice. For instance, 100 gallons of 1% Bordeaux mixture prepared from a stock solution of copper sulphate in which 10 parts of the salt were dissolved in 100 parts water will be only 0.32 pounds too weak, and if the wash were made with a stock solution made by dissolving 20 parts copper sulphate in 100 parts water the error would be 0.6 pounds or 0.075%.

A stock solution containing 20% cupric sulphate can be readily obtained in twelve hours by suspending the salt in a bag of hemp or cheese cloth near the surface of the water. If hot water is used instead of cold, the dissolution of the salt can be obtained within half an hour.

The quicklime used in making Bordeaux mixture should be preferably 90% pure, and as free as possible from carbonate. Magnesian limestone and partially carbonated lime (air-slacked lime) may be used in pre-

paring Bordeaux mixture without affecting to any appreciable extent its chemical composition, but their use is not to be recommended for obvious reasons. The transportation charges and cost of handling per unit of lime are much higher for an impure than a pure lime; as a rule also the unit of lime in the purer quicklime is cheaper than the unit of lime in the poorer quality. Furthermore, the washes thickened by an excess of inert material clog the spray nozzles more frequently, thus entailing, not only an increase in cost of application, but greater wear and tear on the spray machinery, none of which disadvantages are sufficiently compensated for by benefits derived in other ways. To be sure calcic carbonate retards settlement slightly, and magnesic oxide and magnesic carbonate not only retard settlement but delay crystallization, thus extending the time of serviceableness of Bordeaux mixture. However, as retardation of settlement obtained by the addition of inert material can not be considered advantageous from any point of view, and increased serviceableness can be effectively and cheaply obtained by other means, the benefit derived from the use of impure lime can not be considered compensation for the material disadvantages that necessarily follow its use in preparing Bordeaux mixture.

Quicklime is transformed into milk of lime by hydrating (slacking in water), and either cold or hot water may be used for this purpose. When the latter is used, the milk obtained is usually freer from coarse particles, especially is this the case when partly air-slacked or magnesian limestone is used. When hot water is employed there is also little or no danger of "drowning" the lime, but when slacking in cold water some care must be exercised. In the latter case the water should be added to the lime in quantity just sufficient to cover it. As the lime begins to slack, the water will be absorbed with considerable evolution of heat, and a further quantum should be added, and so on as required until the lime becomes pasty, when it may be completely covered. As soon as the milk of lime is prepared, it is ready to be made into a stock solution of lime water, or milk of lime.

Lime water is readily prepared by placing an excess of hydrated lime in water and stirring the mixture a few times for an hour or so, and allowing the non-dissolved salt to settle, and then decanting the supernatant liquid. The non-dissolved calcic hydrate may be used to prepare further amounts of lime water. The proportions of hydrated lime to use for any given quantity of water are not material, provided an excess is assured. The following formula will, however, form a satisfactory working basis: calcic oxide one-half part; water to 100 parts.

The stock solutions of milk of lime are simply prepared by adding to the slacked lime the amount of water required. As Bordeaux mixture may be prepared equally satisfactorily by either of the following methods.

Strong lime to weak copper,
Lime to copper equal strengths,
Weak lime to strong copper,
Lime and copper equal strengths poured together,
Weak copper to strong lime,
Copper to lime, equal strengths,

it is perfectly obvious that the stock solutions of lime can be made up so as to be conveniently used in one or the other of the above methods.

it should be noted that lime water and milk of lime absorb carbon dioxide when exposed to the atmosphere, and must, therefore, be protected as much as possible from its influence. This is more important in the case of lime water, particularly if it has been decanted. If the solutions are not disturbed, however, even in the open air, the film of carbonate that covers their exposed surfaces is quite an efficient protection, though a non-volatile oil forms, of course, a more perfect covering.

SUMMARY

I. Bordeaux mixture may be composed of one or several basic cupric sulphates or mixtures of basic cupric sulphates depending on the ratio cupric sulphate to calcic oxide employed.

II. The copper precipitate of Bordeaux mixtures in which the ratio cupric sulphate to calcic oxide is 1:1 or 1:0.5 becomes crystalline on standing when the washes contain more than 0.125% cupric sulphate. The rate at which the copper precipitate becomes crystalline depends on the temperature and concentration in cupric sulphate of the mixtures.

III. The crystallization of Bordeaux mixtures 1:1 and 1:0.5 is retarded by the presence of such impurities as ferrous sulphate, calcic carbonate, magnesic oxide and magnesic carbonate; but this retardation is not due to the diluent action of the salts in question.

IV. The crystallization of Bordeaux mixtures 1:1 and 1:0.5 may also *ceteris paribus* be delayed by various inorganic salts and organic substances, saccharose being particularly effective.

V. Bordeaux mixtures after carbonization are slightly soluble in pure water, and dissolve readily in water containing carbon dioxide in solution.

VI. Bordeaux mixtures are soluble in water containing ammonic salts in solution.

VII. Alkaline Bordeaux mixtures are soluble in dextrose, saccharose and other organic substances giving the biuret reaction.

VIII. The physical state of the copper precipitate found in Bordeaux mixtures is affected, irrespective of the ratio cupric sulphate to calcic oxide, by:

a. The dilution of the salts and the manner in which they are brought together.

b. The temperature of the water.

IX. After the cupric sulphate and calcic oxide have been brought together, a slight delay in stirring the mixture does not materially affect the physical state of the precipitate.

X. Long continued stirring of Bordeaux mixture does not materially affect the physical state of the precipitate.

XI. The Bordeaux mixtures employed in practice fall into one or another of three types.

a. "Neutral" Bordeaux mixtures of which Woburn Bordeaux mixture is a true type and "acid" Bordeaux mixture a proximate type.

b. Slightly alkaline Bordeaux mixtures. "Neutral" Bordeaux mixture is a good example of this class.

c. Strongly alkaline, or basic Bordeaux mixtures. In this class belong those Bordeaux mixtures in which the ratio cupric sulphate to calcic oxide is not greater than 2 to 1.

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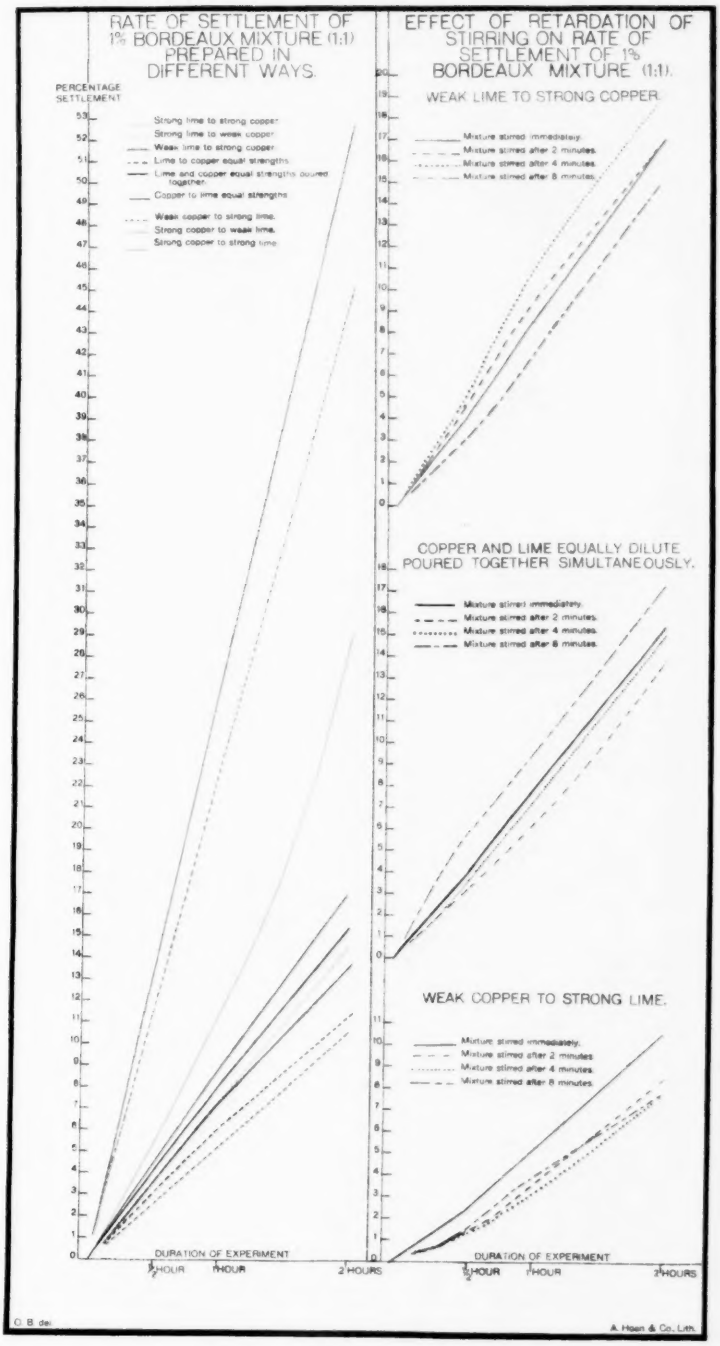
DESCRIPTION OF PLATE VII

Left-hand figure. Graph of rate of settlement of 1% Bordeaux mixtures 1:1 prepared according to each of the nine methods described on page 155 of the text.

Right-hand figure. Graphs showing effect of retardation of stirring on rate of settlement of 1% Bordeaux mixture 1:1. Prepared in different ways.


RATE OF SETTLEMENT OF 1% BORDEAUX MIXTURE (1:1) PREPARED IN DIFFERENT WAYS.
PERCENTAGE SETTLEMENT
Strong lime to strong copper.
Strong lime to weak copper.
Weak lime to strong copper.
Lime to copper equal strengths.
Lime and copper equal strengths poured together.
Copper to lime equal strengths.
Weak copper to strong lime.
Strong copper to weak lime.
Strong copper to strong lime.
DURATION OF EXPERIMENT
½ HOUR
1 HOUR
2 HOURS
EFFECT OF RETARDATION OF STIRRING ON RATE OF SETTLEMENT OF 1% BORDEAUX MIXTURE (1:1).
WEAK LIME TO STRONG COPPER.
Mixture stirred immediately.
Mixture stirred after 2 minutes.
Mixture stirred after 4 minutes.
Mixture stirred after 8 minutes.
COPPER AND LIME EQUALLY DILUTE POURED TOGETHER SIMULTANEOUSLY.
Mixture stirred immediately.
Mixture stirred after 2 minutes.
Mixture stirred after 4 minutes.
Mixture stirred after 8 minutes.
WEAK COPPER TO STRONG LIME.
Mixture stirred immediately.
Mixture stirred after 2 minutes.
Mixture stirred after 4 minutes.
Mixture stirred after 8 minutes.
DURATION OF EXPERIMENT
½ HOUR
1 HOUR
2 HOURS
O. B. del.
A. Hoen & Co., Lith.

BUTLER: BORDEAUX MIXTURE

Description Plate VIII

All the figures are similarly magnified and *only* the copper precipitate is shown. Hence all differences both between and within the figures are differences in the physical state of the copper precipitate.

Fig. 1. Form in which the copper precipitate is obtained when 1% Bordeaux mixture 1:1 is made with water at 10°C.

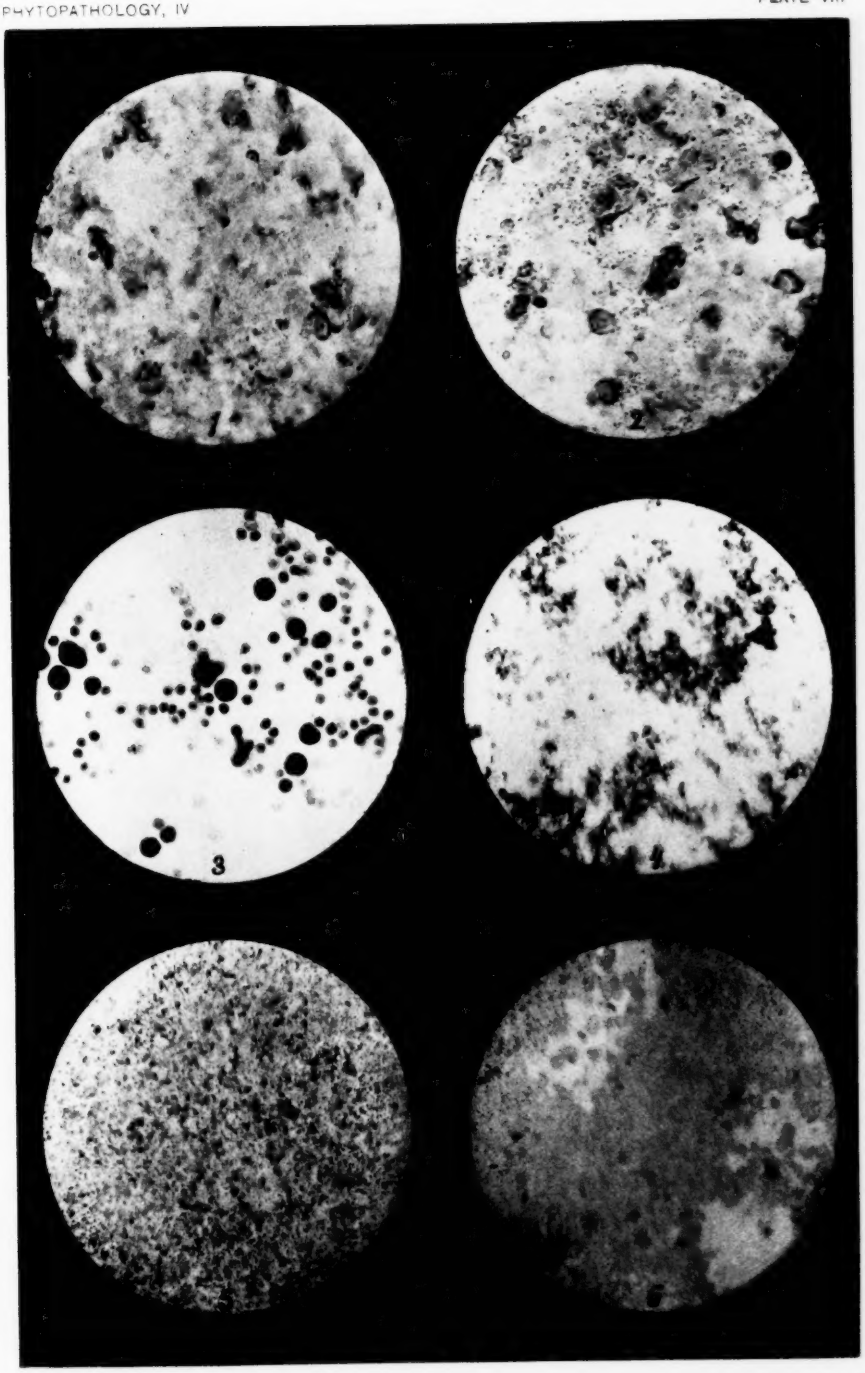
Fig. 2. Form in which the copper precipitate is obtained when 1% Bordeaux mixture 1:1 is made with water at 30°C.

Fig. 3. Deteriorated 1% Bordeaux mixture 1:1. The copper precipitate is entirely in the form of sphaerocrystals.

Fig. 4. Form in which the copper precipitate occurs in 0.125% Bordeaux mixture (1:1) after 151 days at 9°C.

Fig. 5. Form in which the copper precipitate occurs in 1% Bordeaux mixture 1:1 containing 0.015% saccharose after 37 days at 9°C.

Fig. 6. Form in which the copper precipitate occurs in 0.5% Woburn Bordeaux mixture made with lime water at room temperature.



U. S. PHOTO E. O. COCKAYNE COLL.

BUTLER: BORDEAUX MIXTURE

NOTES ON SOME DISEASES OF TREES IN OUR NATIONAL FORESTS. IV[1]

GEORGE GRANT HEDGCOCK

This paper is a continuation of observational notes[2] on forest tree diseases made chiefly by the writer during a disease survey of the western forests of the United States in recent years.

HERPOTRICHIA AND NEOPECKIA

Herpotrichia nigra Hartig, and its related form or species *Neopeckia coulteri* (Peck) Sacc., while not of great importance, are found frequently and only at high altitudes in our western forests. The altitude at which they occur varies from 6000 to 11,000 feet and increases with the elevation at which forest trees may be found. This is the lowest in northwestern United States in the Rocky Mountains and increases to the southward. In Colorado and California these fungi occasionally occur at an elevation of 11,000 feet.

These fungi can not be considered obligate parasites, although they can and do penetrate the tissues of living leaves to some extent and should therefore be considered as somewhat parasitic in their action. The death of the leaves and twigs of the host is caused chiefly by the smothering effect of the dark, dense, felty layers of mycelium shutting out the light and air.

Only small trees or the lower limbs of larger ones that have become buried under heavy layers of snow commonly become diseased. Exceptions may be noted where larger trees are torn or bent down by snowslides and become diseased after being buried under the snow in this manner.

Herpotrichia nigra is known to attack the leaves and twigs of species of Abies, Juniperus, Libocedrus and Picea; *Neopeckia coulteria*, those of species of Pinus.

[1] Published by permission of the Secretary of Agriculture.

[2] Notes on some diseases of trees in our national forests; I, Printed privately at Washington, D. C., February, 1914; II, Phytopathology **2:** 73–80. April, 1912; III, Phytopathology **3:** 111–114. April, 1913.

Sturgis[3] recently published a paper on the occurrence of these fungi in the United States. The following data[4] are in addition to those in Sturgis' paper.

Herpotrichia nigra has either been collected or reported from Colorado, Wyoming, Montana, Oregon and California on *Abies concolor, A. lasiocarpa, A. magnifica, A. shastensis, Juniperus communis, Libocedrus decurrens, Picea engelmanni* and *Tsuga mertensiana* in the following localities:

Colorado

On *Abies lasiocarpa*[5]—Pikes Peak, *A. W. Sampson*, 562; northeast of Steamboat Springs, *Hedgcock*.

On *Picea engelmanni*—near Steamboat Springs, *W. D. Edmondson*, 55; near Gunnison, *W. R. Kreutzer*, 58; near Dillon, *E. R. Hodson*, 1017; near Red Cliff, 848; near Vasquez, 3866; near Steamboat Springs, 3882; near Corona, 3902; in the Uncompaghre Mountains southeast of Delta, 9824, *Hedgcock*.

On *Juniperus communis*—near Goodwin Creek, southwest of Westcliffe, 8109; in the Uncompaghre Mountains, southeast of Delta, *Hedgcock*.

Wyoming

On *Abies lasiocarpa*—near Hahn's Peak, *Edmondson*, 53, 54.

On *Picea engelmanni*—near Hahn's Peak, *Edmondson*, 52.

Idaho

On *Abies lasiocarpa*—near Blodgett's Pass, Bitter Root Mountains, *Hedgcock* and *Weir*, 11225, 11230; near Bonanza (Challis national forest), *Hedgcock*.

On *Picea engelmanni*—near Blodgett's Pass, *Hedgcock* and *Weir*, 11203, 11229.

Oregon

On *Picea engelmanni*—region of Crater Lake, *T. P. Munger*.

On *Tsuga mertensiana*—Crater Lake (Crater national forest), *Meinecke*, D 144.

[3] Phytopathology **3:** 152–158, pls. 12, 13. June, 1913.

[4] Numbers refer to collections for study, Office of Investigations in Forest Pathology.

[5] The nomenclature for trees in this paper is that of Geo. B. Sudworth, U. S. Dept. Agr., Bur. For. Bul. 17. 1898.

California

On *Abies concolor*—Mount Shasta, *Hedgcock* and *Meinecke*, 9638; Huckleberry Meadow (Sequoia national forest); Fort Goff Creek, Siskiyou County, *Meinecke*, D 138; Mount Marble (Klamath national forest), *Hedgcock*.

On *Abies magnifica*—Mount Marble, *Hedgcock*; near Horse Camp, Mount Shasta, *Meinecke*, D 142.

On *Abies shastensis*—Mount Shasta, *Hedgcock* and *Meinecke*, 9639.

On *Libocedrus decurrens*—Huckleberry Meadow (Sequoia national forest); Weston's Camp, Indian Creek, Siskiyou County, *Meinecke*, D 135.

The form known as *Neopeckia coulteri* has either been collected or reported from Utah, Idaho, Oregon and California on *Pinus albicaulis*, *P. balfouriana*, *P. contorta*, *P. flexilis* and *P. monticola* from the following localities:

Utah

On *Pinus albicaulis*—near Horse Camp, Mount Shasta, Siskiyou County, *Meinecke*, D 141.

On *Pinus contorta*—east of Kammas (Uinta national forest), *Hedgcock*, 9853; Tuolumme Meadows (Yosemite national park), *Meinecke*, B 1.

On *Pinus monticola*—head of Applegate Creek, Siskiyou County, *Meinecke*, D 136.

Idaho

On *Pinus albicaulis*—near Blodgett's Pass, *Hedgcock* and *Weir*.

On *Pinus contorta*—near Big Springs, 949; near Bonanza, 9390, *Hedgcock*.

On *Pinus flexilis*—near Bonanza, 9391, *Hedgcock*.

Oregon

On *Pinus contorta*—Rosland, Crook County, *Munger*, 56, 57; south of St. Helen, and in the Crater Lake region, *Munger*.

California

On *Pinus contorta*—near Big Meadow (Sequoia national forest); near Cliff Camp and Graveyard Meadow (Sierra national forest), *Meinecke*.

On *Pinus balfouriana*—Moraine Creek (Sequoia national forest) *Meinecke*.

For *Herpotrichia nigra*, *Abies magnifica*, *A. shastensis*, *Juniperus communis*, *Libocedrus decurrens* and *Tsuga mertensiana* are new hosts; for *Neopeckia coulteri*, *Pinus albicaulis*, *P. balfouriana*, *P. flexilis* and *P. monticola* are new.

FOMES PINICOLA

Under *Fomes pinicola* Fr. is included *Fomes ungulatus* (Schaeff.) Sacc., *Fomes marginatus* Gill., and *Polyporus ponderosus* Schrenk which represent different forms of the species. This fungus is considered the most important of those attacking both standing and fallen tree trunks of conifers. It not only attacks coniferous wood but also frondose wood of a number of species.

Fomes pinicola attacks living trees to some extent, gaining entrance through wounds. It may enter through heartwood or sapwood, as it rots both readily. It is one of the most widely distributed species in the United States, occurring, so far as has been observed, in every region where conifers are found.

Fomes pinicola has either been reported or collected on the following coniferous trees in the United States: *Abies amabilis, A. arizonica, A. concolor, A. grandis, A. lasiocarpa, A. magnifica, A. nobilis, A. shastensis, Pinus albicaulis, P. aristata, P. arizonica, P. attenuata, P. cembroides, P. chihuahuana, P. contorta, P. divaricata, P. echinata, P. edulis, P. flexilis, P. glabra, P. jeffreyi, P. lambertiana, P. mayriana, P. monophylla, P. monticola, P. palustris, P. ponderosa, P. resinosa, P. rigida, P. sabiniana, P. strobiformis, P. strobus, P. taeda, P. virginiana, Larix laricina, L. lyalli, L. occidentalis, Picea canadensis, P. engelmanni, P. mariana, P. parryana, P. rubens P. sitchensis, Pseudotsuga taxifolia, Tsuga canadensis, T. heterophylla* and *T. mertensiana.*

Fomes pinicola has been collected or reported on other host species, not coniferous, in the United States as follows: *Acer saccharinum, Alnus oregona, A. tenuifolia, Betula fontinalis, B. lenta, B. lutea, B. occidentalis, B. papyrifera, Fagus atropunicea, Magnolia foetida, Populus balsamifera, P. grandidentata, P. tremuloides, P. trichocarpa, Prunus serotina.*

On the majority of the preceding host species, *Fomes pinicola* is now reported for the first time. On frondose wood, it has been found chiefly in moist regions in the northern and south central United States. In the drier regions it rarely is found fruiting on frondose wood.

The rot caused by *Fomes pinicola* is primarily one of the sapwood, although at rare intervals an instance may be noted of the decay it produces originating in the heartwood of conifers. The color of the decayed sapwood is usually yellow to yellow-brown, depending, as a rule, upon the original color of the wood before decay sets in. That of the heartwood is yellow-brown to brown, varying for the same reason. The rotten wood in the final stages of decay, especially where exposed to air breaks up into small cubical pieces, very much smaller than those in wood rotted by *Polyporus schweinitzii* Fr.

FOMES FOMENTARIUS

Fomes fomentarius (L.) Fries is almost as widely distributed in the United States as the beeches and birches it commonly attacks. It causes primarily a rot of the sapwood of trees, and secondarily may attack the heartwood. The sporophores are found as a rule on dead trees, but occasionally are found on living trees, the fungus having gained entrance through wounds. The fungus produces a rot of a light yellow or creamy white color, not differing greatly from the color of the wood before it is decayed.

Fomes fomentarius has been either collected or reported in the survey as follows: On *Acer saccharum*, *A. saccharinum*, *Betula fontinalis*, *B. occidentalis*, *B. papyrifera*, *Fagus atropunicea*, *Populus tremuloides*, *P. trichocarpa*, *Prunus serotina*, *Quercus digitata* and *Q. nigra*. Its known range in the United States is from Maine to Washington and Oregon, and southward to the Gulf of Mexico in the eastern portion of the country.

FOMES APPLANATUS

A large number of host species of trees attacked by *Fomes applanatus* (Pers.) Wallr. are given in a previous paper, III, of this series. After making further studies concerning the effect of this fungus upon living trees, the writer has come to the conclusion that very frequently it attacks both the sapwood and heartwood of many living trees. It is able to enter such trees only through wounds. In the majority of instances, however, the fungus acts only as a saprophyte.

In the Manti national forest near Ephraim, Utah, in 1912, *Fomes applanatus* was found by the writer to be the cause of a serious root-rot of the aspen (*Populus tremuloides*). The disease also extended a short distance into the butts of the trees. In many instances the fungus was observed fruiting at the base of living trees. In such cases it is apparently able to kill the tissues of the cambium to some extent in the region of most acute attack. The loss caused by this fungus is considerable on moist slopes in this forest. It is not so common in drier localities in the same region. A similar effect of this fungus has previously been noted by the writer elsewhere in western forests, for example, in the Sandia Mountains, New Mexico, but the fungus in such cases was usually preceded by *Fomes igniarius* which apparently weakened the trees before the former fungus gained an entrance. In the Manti forest, on the other hand, *Fomes igniarius* rarely attacks the aspen, especially in the locality where the outbreak of *Fomes applanatus* was found.

Fomes applanatus, or a very closely related species, is known to attack the heartwood of oaks. The writer has repeatedly found maples and

oaks, especially *Acer saccharinum*, and *Quercus rubra*, badly injured by this fungus. Many old shade trees suffer from the action of this fungus on the heart and sapwood.

The following additional hosts for *Fomes applanatus* have been noted in the survey: *Abies balsamea*, *Acer rubrum*, *Betula lenta*, *B. nigra*, *B. papyrifera*, *Crataegus coccinea*, *Nyssa sylvatica*, *Populus alba*, *P. fremontii wislizeni*, *P. heterophylla*, *Pyrus malus* and *Quercus pagodaefolia*.

POLYPORUS SCHWEINITZII

The most important root-rotting fungus of conifers is *Polyporus schweinitzii* Fr. It also extends into the butts of trees, producing a serious rot of the first saw log or cut. This fungus is apparently found wherever pines occur in the United States although not reported from many localities, and not from all species of pines. The Douglas fir (*Pseudotsuga taxifolia*) when nearly mature is especially susceptible to the heart rot caused by this fungus. Data collected by the writer indicate that usually more trees of this species are attacked by *Polyporus schweinitzii* than by any other heart-rotting fungus. The number of diseased trees, estimated from stumps or saw logs, in forests in Idaho, Montana, and Oregon was found to be from 5 to 30 per cent of the total cut. This did not include trees too badly diseased for cutting. This fungus is more common than *Trametes pini* on this host in many localities in southern Montana. In moist valleys in western Oregon and Washington, however, the latter fungus more commonly attacks the Douglas firs in mature stand, and among very old trees all are diseased and worthless, owing to the fact that *Trametes pini* rots the heart of the trunk in such cases throughout its length. Since the rot caused by *Polyporus schweinitzii* is almost universally confined to the roots and base of the trunk of the trees it attacks, it frequently happens in northwestern forests that trees are attacked by both species; by the latter at the base, and by the former higher up. A later publication will treat of this subject more fully.

The red-brown rot of *Polyporus schweinitzii* has been reported in the survey in the following additional host species: *Abies magnifica*, *A. nobilis*, *Larix lyalii*, *Picea canadensis*, *P. mariana*, *P. parryana*, *Pinus attenuata*, *P. cembroides*, *P. chihuahuana*, *P. edulis*, *P. glabra*, *P. jeffreyi*, *P. mayriana*, *P. monophylla*, *P. rigida*, *P. sabiniana*, *Picea rubens* and *Thuja plicata*.

FOMES ROSEUS

Fomes roseus (Fr.) Cooke (*Polyporus carneus* Nees) is another widely distributed fungus which ordinarily is found on the wood of conifers, but

may also attack frondose wood. Von Schrenk[6] has already published concerning a disease of junipers caused by this fungus. His observations regarding the disease have been verified by Carl Hartley of this office, and also by the writer.

The writer finds that *Fomes roseus* as known at present has a wide range of hosts. There are two forms of sporophores, one with thin and the other with thick bracket-shaped fruits, the latter tending to become hoof-shaped. Both forms differ widely in size, depending largely on the substratum upon which they grow. The largest sporophores of the latter type were found by the writer on the heartwood of a trunk of an Engelmann spruce in Colorado a few months after it was cut down. The tree was alive when cut, and was diseased with a pocketed rot much like the one found in *Juniperus virginiana* as described by von Schrenk. The same disease has been found by the writer in a number of western species of juniper and a similar rot occurs in the cedars in northwestern United States. In the latter case, owing to the similarity of the rot, in some cases, to that caused by *Polyporus schweinitzii*, unless sporophores are present the cause may not be known with certainty. The rot caused by *Fomes roseus* is dark brown only in case the heartwood is of a brownish color before decay takes place, and it may be lighter in color corresponding to the texture and color of the wood attacked. The sporophores of the fungus are usually found on dead wood on dead areas on living trees. *Pseudotsuga taxifolia* is the usual host for this fungus in the west, but it is also found frequently on spruces and pines.

The characteristic rot, or the sporophores, of *Fomes roseus* have either been reported or collected in the survey as follows: On *Abies balsamea, A. shastensis, Acer rubrum, Juniperus californica, J. monosperma, J. occidentalis, J. pachyphloea, J. sabinoides, J. utahensis, J. virginiana, Larix laricina, L. occidentalis, Picea canadensis, P. engelmanni, P. mariana, P. parryana, P. rubens, P. sitchensis, Pinus arizonica, P. contorta, P. divaricata, P. flexilis, P. ponderosa, P. resinosa, P. strobus, P. strobiformis, P. virginiana, Amygdalus persica, Pseudotsuga taxifolia, Tsuga canadensis* and *T. heterophylla.*

The fungus has been reported from thirty-one states, indicating that its distribution is general in the United States. These states represent every important forest in the United States from near sea level to an elevation of 10,000 feet.

Prof. E. T. Harper has in his private herbarium a specimen of *Fomes roseus* collected on *Betula papyrifera* from Isle Royale, Michigan. This with specimens collected by Carl Hartley on *Amygdalus persica* at Wash-

[6] U. S. Dept. Agr. Div. Veg. Phys. and Path. Bul. 21: 16–21. 1900.

oaks, especially *Acer saccharinum*, and *Quercus rubra*, badly injured by this fungus. Many old shade trees suffer from the action of this fungus on the heart and sapwood.

The following additional hosts for *Fomes applanatus* have been noted in the survey: *Abies balsamea, Acer rubrum, Betula lenta, B. nigra, B. papyrifera Crataegus coccinea, Nyssa sylvatica, Populus alba, P. fremontii wislizeni, P. heterophylla, Pyrus malus* and *Quercus pagodaefolia.*

POLYPORUS SCHWEINITZII

The most important root-rotting fungus of conifers is *Polyporus schweinitzii* Fr. It also extends into the butts of trees, producing a serious rot of the first saw log or cut. This fungus is apparently found wherever pines occur in the United States although not reported from many localities, and not from all species of pines. The Douglas fir (*Pseudotsuga taxifolia*) when nearly mature is especially susceptible to the heart rot caused by this fungus. Data collected by the writer indicate that usually more trees of this species are attacked by *Polyporus schweinitzii* than by any other heart-rotting fungus. The number of diseased trees, estimated from stumps or saw logs, in forests in Idaho, Montana, and Oregon was found to be from 5 to 30 per cent of the total cut. This did not include trees too badly diseased for cutting. This fungus is more common than *Trametes pini* on this host in many localities in southern Montana. In moist valleys in western Oregon and Washington, however, the latter fungus more commonly attacks the Douglas firs in mature stand, and among very old trees all are diseased and worthless, owing to the fact that *Trametes pini* rots the heart of the trunk in such cases throughout its length. Since the rot caused by *Polyporus schweinitzii* is almost universally confined to the roots and base of the trunk of the trees it attacks, it frequently happens in northwestern forests that trees are attacked by both species; by the latter at the base, and by the former higher up. A later publication will treat of this subject more fully.

The red-brown rot of *Polyporus schweinitzii* has been reported in the survey in the following additional host species: *Abies magnifica, A. nobilis, Larix lyalii, Picea canadensis, P. mariana, P. parryana, Pinus attenuata, P. cembroides, P. chihuahuana, P. edulis, P. glabra, P. jeffreyi, P. mayriana, P. monophylla, P. rigida, P. sabiniana, Picea rubens* and *Thuja plicata.*

FOMES ROSEUS

Fomes roseus (Fr.) Cooke (*Polyporus carneus* Nees) is another widely distributed fungus which ordinarily is found on the wood of conifers, but

may also attack frondose wood. Von Schrenk[6] has already published concerning a disease of junipers caused by this fungus. His observations regarding the disease have been verified by Carl Hartley of this office, and also by the writer.

The writer finds that *Fomes roseus* as known at present has a wide range of hosts. There are two forms of sporophores, one with thin and the other with thick bracket-shaped fruits, the latter tending to become hoof-shaped. Both forms differ widely in size, depending largely on the substratum upon which they grow. The largest sporophores of the latter type were found by the writer on the heartwood of a trunk of an Engelmann spruce in Colorado a few months after it was cut down. The tree was alive when cut, and was diseased with a pocketed rot much like the one found in *Juniperus virginiana* as described by von Schrenk. The same disease has been found by the writer in a number of western species of juniper and a similar rot occurs in the cedars in northwestern United States. In the latter case, owing to the similarity of the rot, in some cases, to that caused by *Polyporus schweinitzii*, unless sporophores are present the cause may not be known with certainty. The rot caused by *Fomes roseus* is dark brown only in case the heartwood is of a brownish color before decay takes place, and it may be lighter in color corresponding to the texture and color of the wood attacked. The sporophores of the fungus are usually found on dead wood on dead areas on living trees. *Pseudotsuga taxifolia* is the usual host for this fungus in the west, but it is also found frequently on spruces and pines.

The characteristic rot, or the sporophores, of *Fomes roseus* have either been reported or collected in the survey as follows: On *Abies balsamea, A. shastensis, Acer rubrum, Juniperus californica, J. monosperma, J. occidentalis, J. pachyphloea, J. sabinoides, J. utahensis, J. virginiana, Larix laricina, L. occidentalis, Picea canadensis, P. engelmanni, P. mariana, P. parryana, P. rubens, P. sitchensis, Pinus arizonica, P. contorta, P. divaricata, P. flexilis, P. ponderosa, P. resinosa, P. strobus, P. strobiformis, P. virginiana, Amygdalus persica, Pseudotsuga taxifolia, Tsuga canadensis* and *T. heterophylla.*

The fungus has been reported from thirty-one states, indicating that its distribution is general in the United States. These states represent every important forest in the United States from near sea level to an elevation of 10,000 feet.

Prof. E. T. Harper has in his private herbarium a specimen of *Fomes roseus* collected on *Betula papyrifera* from Isle Royale, Michigan. This with specimens collected by Carl Hartley on *Amygdalus persica* at Wash-

[6] U. S. Dept. Agr. Div. Veg. Phys. and Path. Bul. 21: 16–21. 1900.

ington, West Virginia, and by the writer on *Acer rubrum* at Takoma Park, Maryland, are the only collections known by the writer to have been made on frondose wood.

The wood decay caused by this fungus takes the pocket form in living juniper and spruce trees, and probably also in living trees of other host species mentioned in preceding paragraphs. In many cases, where found on dead logs and fallen trees, both the sapwood and heartwood are rotted by the fungus.

OFFICE OF INVESTIGATIONS IN FOREST PATHOLOGY
UNITED STATES DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

CLADOSPORIUM DISEASE OF AMPELOPSIS TRICUSPIDATUM

MEL. T. COOK AND GUY WEST WILSON

WITH ONE FIGURE IN THE TEXT

During the summer of 1913 the writers' attention was called to the dying of *Ampelopsis tricuspidata* on the buildings of Rutgers College and other buildings in this vicinity. The buildings in question were covered by a large number of vines growing very close together, which had been set by graduating classes for a number of years past. A careful examination showed that many of these vines of all ages were dead. The disease first appeared as a wilting of leaves which might be confined to a small branch or might extend to a main trunk and all its branches. Within a few days all the diseased parts were dead and dry. Sections cut from these vines and put into moist chambers developed a growth of mycelium within 24 to 48 hours. Within three days this growth became very abundant and was apparently a single organism. This was transferred to plates and tubes from which later inoculations were made into healthy vines. Within about ten days these vines showed the first effects of the disease and later cultures from them gave the same organism.

In about two weeks the section of vines in the moist chambers showed an abundance of olive-colored pustules about a millimeter in diameter which were composed entirely of fertile hyphae of a species of Cladosporium. Similar bodies were found on last years' peduncles and mummied berries of both diseased and healthy vines.

The hyphae like those of other species of Cladosporium are rather indefinite in manner of branching, multi-septate and brownish in color. The fertile regions have knot-like processes on which the conidia are borne. They are strikingly similar to *C. fulvum* Cooke which occurs on tomato leaves. The conidia are extremely variable both in size and form, ranging from spherical to eliptical or oval. They may be continuous but are usually uniseptate, occasionally biseptate. The smaller conidia are about 4 to 6 μ in diameter, while the elongate ones are 4 to 8 x 9 to 20 μ.

The fungus appears to be a saprophyte, becoming parasitic under exceptional conditions. As previously stated, the vines are growing very close together and in very poor red shale soil. These conditions, together with the extremely dry summer, may account for a weakened vitality of the vines allowing the fungus to overcome them. Inquiry of persons who

have been connected with the College for a number of years brought out the information that similar outbreaks had occurred in past years. This was also confirmed by the fact that many old vines an inch or more in diameter were found to be dead and partially rotten.

The organism has been referred to *Cladosporium herbarum* Link (Kellerman Ohio Fungi No. 124). Von Thümen has recorded the same species on the grape vine in Europe. There is a specimen of the same fungus in the New York Botanical Garden, collected by Newton B. Pierce on grapes in California. A similar fungus on the grape has been described from Australia by McAlpine as *C. uvarum*. Of this fungus its author says, "This species forms dense nodules, sometimes 2 mm. thick in the interior of the grape, which is dried up. It differs from the common and very variable *C. herbarum* Link in forming these nodular massse and in the presence of numerous resting-bodies" (McAlpine, Add. Fungi Vine Australia, 47, 1890). As these characteristics are not present in our fungus, we need not consider *C. uvarum* further.

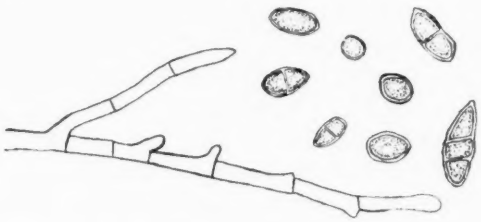


FIG. 1. Conidiophore and conidia of Cladosporium from Ampelopsis.

The fungus on Ampelopsis agrees with the rather loose characterization which is usually given to *C. herbarum*. However, the conidiophores have very pronounced lateral enlargements on which conidia are borne. These are larger than in any other form of the species which has come to our notice, yet it does not seem wise at present to separate this form as a new species. The great diversity of forms recognized by Saccardo as belonging to this species, and the range of hosts on which it has been reported as being parasitic, would indicate that it is a fruitful field for investigation.

While this species has usually been considered saprophytic, yet recent investigations by Kosmahl, Lopriore and Janczewski have attributed several diseases to its activities. Among these diseases is the black head of grain which was very abundant in New Jersey during the past summer.

RUTGERS COLLEGE
NEW BRUNSWICK, NEW JERSEY

PATHOLOGICAL HISTOLOGY OF THE ENDOTHIA CANKER OF CHESTNUT[1]

W. E. KEEFER

WITH THREE FIGURES IN THE TEXT

The changes produced in bark and sapwood of *Castanea dentata* when invaded by *Endothia parasitica* have received little attention from pathologists. The investigations recorded below were undertaken with a view to determining the nature of such changes by a comparative study of the anatomy and histology of normal and diseased tissues from stems of one year's growth and sections of the bark and sapwood from trees quite mature. Free-hand sections of fresh material were used when possible; but sections requiring more uniformity and permanency were made by means of a sliding microtome, the sections of the tissue having been previously imbedded in celloidin. Paraffin material is unsuitable, because of the extreme hardness of the tissue. There were a number of staining combinations used to bring out the various tissues. The different conditions are described below. A brief description of the structure of the normal tissues is first given and then the changes that have taken place due to the invasion of the fungus.

THE PRIMARY CORTEX

Under this heading is included all the tissue from the cork tissue on the extreme outside of the stem to the innermost internal cork layer of the pericycle. The tissues comprise the cork tissue on the extreme outside of the stem, the collenchyma which lies next internally, the thin-walled parenchymatous cells, and the bast fibers which are scattered throughout the primary cortex. In older trees the primary cortex is often sloughed off, exposing the internal cork layers.

The cork tissue

Normal. The cork zone completely surrounds the stem, the epidermis having been destroyed in the natural processes of growth of the tree at a very early period. The zone is approximately seven layers of cells in thick-

[1] Investigations carried out under the direction of the Pennsylvania Chestnut Tree Blight Commission.

ness, the individual cells being in uninterrupted connection with one another, and arranged in rows parallel to the surface. These cells are flat, plate-like, in the majority of cases broader than long, with highly suberized walls and reddish brown cell contents which consist of phlobaphenes or tannin compounds.

Diseased. Little or no change can be noticed in this tissue. The walls of the individual cells remain highly suberized and no change in thickness was observed. The walls seem to withstand all attacks of the fungus, and no hyphae were seen penetrating the cell walls or passing between them. By microchemical tests it was observed that the cell contents remain unchanged, both in character and quantity. The shape and size of the cells also remain constant. About the only change to be observed is with respect to the arrangement of the tissue. At points where the pycnidia are forming beneath this tissue, there is a bulging of the outer cork zone, followed by a complete rupture during the maturation of the fruit bodies. From the study of a great many sections of this tissue, the conclusions may be safely drawn that cork cells are practically unaffected by the fungus, with the exception of the rupture which is apparently produced by mechanical pressure from below.

Collenchyma

Normal. Just beneath the cork tissue are the cells of the collenchyma, which are united so as to form a strengthening zone around the stem. The walls of these cells are pure cellulose, thickened generally at the angles, and are in uninterrupted connection with one another. The cells vary greatly in shape and contain chiefly chloroplasts, although there are also quantities of starch, tannins, and crystals of calcium oxalate. The chief functions are to strengthen the stem, provide for slow conduction, for temporary storage of food materials, and for the manufacture of food.

Diseased. With regard to the arrangement of the cells in the diseased stem no changes are noticeable except that where the fruit bodies of the fungus are formed there is a crowding of all the tissues and a disintegration of the cells. By microchemical tests it was determined that a process of lignification takes place in the walls upon the invasion of the fungus, but whether this is a total lignification or not remains to be proven by investigation. This lignification takes place a short distance back of the advancing edge, since it is not apparent in cell walls at the exact edge of the canker. Microchemical tests for lignin were also tried on collenchyma which had been invaded by *Melanconis modonia*, but no reaction for lignin was obtained, indicating that this process of lignification may be peculiarly connected with the fungus *Endothia parasitica*. The cell walls seem to be

easily broken by the fungus, but no hyphae were seen penetrating them. The action of the advancing mycelial mats seems to be physical rather than chemical, and the cells are mechanically broken to pieces. There is a tendency for the chloroplasts to group themselves in clumps, their general arrangement being in contrast to that in the normal cells. There is also a decided diminution of starch within these cells, and a great increase of tannins. The crystals of calcium oxalate remain unchanged. The number and size of the cells remain constant.

Thin-walled parenchyma

Normal. The thin-walled parenchyma lies just beneath the collenchyma. The cells of this tissue are irregular in shape and have no definite

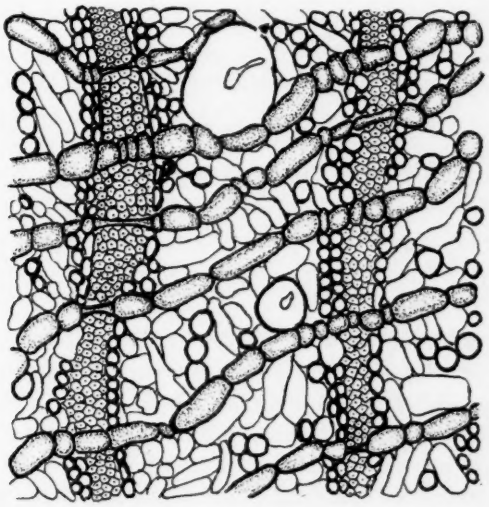


FIG. 1. The mycelial fans in a longitudinal section of diseased bark.

arrangement in layers. There are large intercellular spaces between them. The cell walls are wavy in outline and are composed of pure cellulose. They enclose a very delicate protoplasmic sac. A watery sap fills the whole lumen and within this sap are small amounts of starch and proteid material, and also deposits of calcium oxalate in the form of crystals.

Diseased. As was the case with the collenchyma, the cell walls of this tissue also become lignified when attacked by the fungus, but the process of lignification is not complete, since portions of the walls remain pure cellulose. No hyphae were seen penetrating the cell walls, although masses of the fungus were observed within these cells. The fungus seems to ad-

vance through this tissue by the compact masses of mycelium forcing apart and destroying the cells. This invasion is accompanied by an increase of tannin materials within the cells and a diminution of starch.

Sclerenchyma

Normal. There are two kinds of sclerenchymatous tissue in this stem, namely, the long elements or bast fibers and the short elements or stone cells. The bast fibers are elongated, spindle-shaped cells with highly lignified walls which enclose a very narrow empty cell lumen. The stone cells are short, of irregular shape, and have highly lignified walls, with pits and definite markings. There is a small lumen which contains merely air. These stone cells are without any definite arrangement into layers.

Diseased. These cells are not affected by the fungus, the structure, size, arrangement, and chemical nature being unchanged.

THE PERICYCLE

The term "pericycle" is applied to the tissues which lie between the primary cortex and the bast zone. This includes the successively-formed layers of cork, the sclerenchyma which is made up of bast fibers and stone cells, the parenchyma, and the crystal-containing cells.

The internal cork layers

Normal. The individual cork cells making up the internal successively-formed cork layers are in most respects similar to those described under primary cortex. They are flat, tabular cells which are elongated in the longitudinal and transverse directions and have suberized walls which are in unbroken connection with one another. They make up the cork layers in this portion of the stem, which vary in thickness but usually are composed of twelve to sixteen layers. The arrangement of these internal cork layers is decidedly irregular, branching occurring in all directions in the majority of cases. The cell contents are chiefly tannin compounds.

Diseased. As in the cork cells of the primary cortex, very few changes are to be noticed here. The cell walls, contents, shape, and size remain unchanged. No hyphae were seen penetrating the cell walls. It was observed, however, that masses of mycelium were forcing apart these layers of cork cells, and, as the fan-shaped mycelium advances, a wedging process takes place, splitting the layers of this tissue. Nothing was observed that would indicate that the fungus excretes an enzyme, since this derangement of layers seems to be a purely mechanical process. The individual cells remain practically unchanged. The mycelium of the fungus shows a tend-

ency to follow the layers of cork, for wherever there are cork layers in the diseased portion of the stem, there are also masses of the mycelium in varying amounts, the exact reasons for this fact remaining for further research.

Sclerenchyma

Normal. The bast fibers and the stone cells of the sclerenchyma in the pericycle are the same in structure, general arrangement, size, shape, and contents as the sclerenchyma of the primary cortex.

Diseased. This tissue in diseased stems remains practically unchanged and shows no effects whatever from the invasion of the fungus. The walls remain strongly lignified, and are not penetrated by the mycelium, neither are they broken down.

Parenchyma

Normal. The parenchymatous cells in this portion of the stem differ little from the parenchymatous cells of the primary cortex. The cell walls are mostly cellulose, uniformly thickened and are somewhat lignified in the process of secondary thickening. They are elongated in a tangential direction, forming the so-called "dilational bands" described by De Bary.

Diseased. This tissue is readily affected by the fungus. With respect to the contents of the cells, there is a decided increase of tannin on the invasion of the fungus and a diminution of starch. The cell walls become further lignified but not sufficiently to make themselves immune like the bast fibers, as they are soon disintegrated. The mycelium afterward advances into the cells and occupies them. Whether the fungus disintegrates these cell walls by means of an enzyme is not apparent, but it appears to be a mechanical rather than a chemical process. With regard to the arrangement of the cells it may be stated that the "dilational bands" are badly deranged, entirely losing their identity.

Crystal-containing cells

Normal. These are small cubical cells which have regular, cellulose walls, partially lignified, and a small cavity containing a large crystal of calcium oxalate. They are arranged in precise, regular rows, the individual cells being in uninterrupted connection with one another. These rows of cells have no definite arrangement in continuous zones, but the regular rows are scattered throughout the pericycle.

Diseased. The cells remain unaffected when the pericycle is invaded by the fungus, there being no change in the cell walls, cell contents, shape, size, or arrangement.

THE BAST ZONE

The bast zone lies directly between the pericycle and the cambium layer and is chiefly composed of sclerenchyma in the form of bast fibers, although this portion of the stem also contains sieve tubes, phloem parenchymal, medullary rays, and crystal-containing cells.

The sieve tubes

Normal. The sieve tubes old and new, are scattered throughout this zone without any definite arrangement into layers and are elongated tubes with cellulose walls. On the terminal faces of these tubes are sieve plates which are pitted and lie directly over one another thus furnishing a communication between the different members. They are rich in starch and proteids and also have small amounts of tannin.

Diseased. The walls of these tubes are easily broken by the advancing fungus. They are at first partially lignified and then, by a process which seems to be a physical one, the walls are broken and the mycelium advances in masses and occupies the tubes. There is a diminution of starch and proteids, and an increase of tannin materials within these tubes.

Phloem parenchyma

Normal. When observed in cross section the phloem parenchyma cells are regular and rectangular and in a longitudinal section they appear barrel-shaped. They have pure cellulose walls containing proteids, starch, and also small amounts of tannin. They are arranged in definite rows and are closely connected with the sieve tubes, being capable of serving the function of translocation of carbohydrates when there is a surphus in these tubes.

Diseased. The walls of the cells of this tissue become entirely lignified under the influence of the fungus. Mycelium was observed occupying the cells but there is little doubt that the walls were broken down before the mycelium advanced into the cells, since at no time were any hyphae observed penetrating the cell walls. As in the tissues described above, there was observed a diminution of starch, an increase of tannin compounds, and a decided decrease of proteid material.

Sclerenchyma

Normal. This tissue is the main constituent of the bast zone, and is arranged in definite segmented zones with the large medullary rays extending through them. These zones are mostly made up of bast fibers, although there are also a considerable number of shorter sclerenchymatous elements or stone cells. They are arranged so as to form a cylinder around

the stem, broken only at intervals by the medullary rays. There are a number of layers of this tissue, these being separated from one another by the parenchymatous cells, and the sieve tubes with their accompanying companion cells. The structure of these bast fibers and stone cells has been stated previously.

Diseased. No changes of importance are noticed in this tissue. The individual cells remain unmodified with walls greatly lignified and entire,

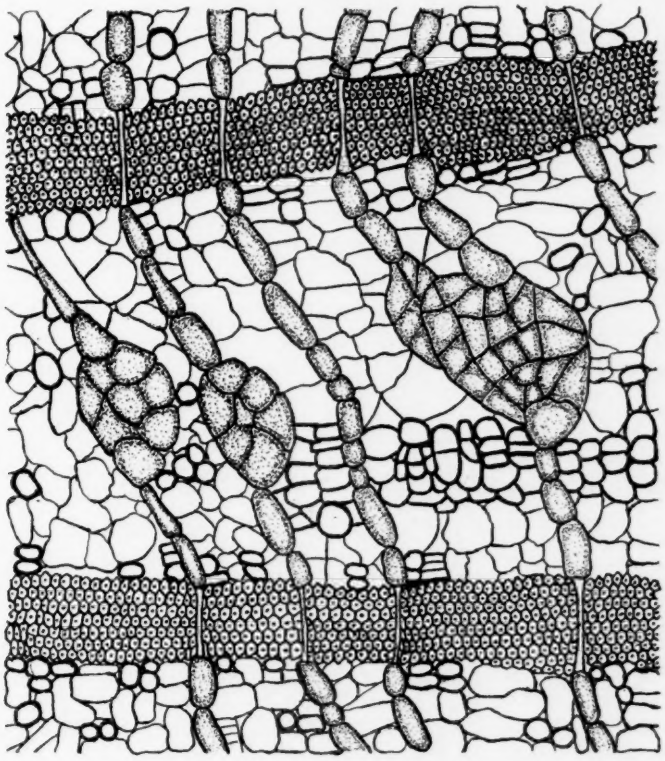


FIG. 2. Cross section of normal bark showing the medullary rays of the bast zone.

as mentioned above with respect to the other bast fibers in the stem. So also the bast fibers in this zone appear to be unaffected by the fungus. The segmental areas are thrown out of arrangement, due to the hyperplasia of the medullary ray cells which extend through them.

Medullary rays

Normal. The cells making up the medullary rays in the bast zone of the stem are unusually large as compared with the cells of other tissues.

They are closely joined to one another and have a very crooked course through the bast zone. The walls are mostly pure cellulose although lignin may be found in small amounts. The cells contain starch, proteids, a very small amount of tannin, and sometimes crystals of calcium oxalate. They are elongated greatly in the transverse and longitudinal directions.

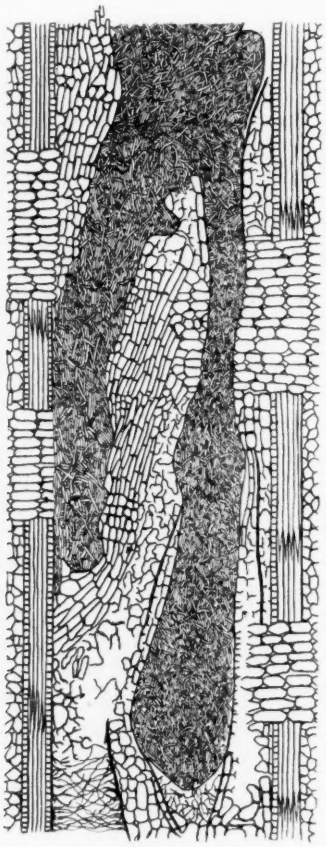


FIG. 3. Cross section of diseased bark showing the abnormal development of the medullary ray cells of the bast zone.

Diseased. A partial process of lignification takes place also in these cells when they are approached by the mycelium, but otherwise they are not individually affected in any way and do not become broken up. No hyphal threads of mycelium were observed in any of these cells. The cell content remains about the same, no changes having been observed with respect to the amounts of tannin, starch, or proteids. It was observed

that there was an increase in the number of medullary ray cells, due probably to some stimulus which the fungus exerts on this tissue. The original cells divide and redivide until great masses of these new cells are formed, which contain starch, proteids, and small amounts of tannin. They have a tendency to form globose cell aggregates and in places they have so multiplied as to almost completely exclude the sieve tubes with their companion cells. There is also a crowding of the phloem parenchyma and a radial and tangential separating of the separate cylinders of the bast zones, due to the hyperplasia of the original ray cells. The walls of these new cells are pure cellulose, and whether a process of lignification ever takes place later has not been determined.

THE CAMBIUM

Normal. Between the xylem and the bast zone, is the cambium which is made up of meristametic, rectangular cells, elongated in a tangential direction. The walls are mostly cellulose except those bordering on the woody portion of the stem. These may be partially lignified. The cells form a continuous zone around the stem and are constantly adding new wood elements to the inside and phloem to the outside. They contain granular protoplasm and single large nuclei. There are also present proteids, tannins, and starch in varying amounts.

Diseased. A partial lignification takes place upon the invasion of the fungus. No hyphae were seen penetrating the cell walls or going between them. As the fan-shaped mycelium advances the cambial cell walls become badly broken and finally completely destroyed. There was observed a diminution of starch and proteids, while the amount of tannin was increased.

THE XYLEM

Since no mycelium was observed in the wood, an experiment was made to determine whether the fungus really does penetrate into the wood and if so, to what depth. The following method was used: Logs were selected and a permanent record was made showing the date of collection, the size of the canker, the approximate age of the limb or trunk, and the details of the isolations. The logs were halved as near as possible to the center of the canker and the exposed surface passed through the flame of an alcohol lamp to guard against contaminations. By means of a steel drill, a small layer of the wood was taken from the top and discarded. The deeper drillings, only, were used for the isolations. These were placed on potato agar slants. If a positive result was obtained in certain slants, another isolation was made from the same log at the same depth and the result thus checked. Following are the results:

SIZE OF CANKER IN MILLIMETERS	DIAMETER OF WOOD PORTION IN MILLIMETERS	APPROXIMATE AGE OF TREE IN YEARS	NUMBER OF RINGS OF POSITIVE ISOLATION	DEPTH OF POSITIVE ISOLATION IN MILLIMETERS
Girdled	70	14	1	1
21 x 120	45	12		
Girdled	80	14		
Girdled	50	12	2	2
Girdled	34	14		
Girdled	47	13	6	10
Girdled	27	7	7	12
Girdled	54	11	2	2
Girdled	49	13		
Girdled	81	13	3	6
140 x 55	56	8	1	2.5
143 x 73	41	7	1½	2.5
160 x 40	41	7	1	1
150 x 45	43	7	1	1.5
210 x 95	47	7	1	1.5
145 x 90	48	7	3	6
150 x 92	42	7	3½	7
90 x 30	42	7	5	9
120 x 90	55	8	1½	2
125 x 75	50	8	1	2
160 x 65	48	8	1	2
260 x 160	180	36	3	6
Girdled	120	22	1½	3

The majority of the trees were badly diseased and were alive when cut. From the foregoing table an average depth of penetration for the entire number of logs was 4.1 mm. or approximately $\frac{1}{8}$ inch. The greatest depth of penetration was 12 mm. or about $\frac{1}{2}$ inch. An average of the diameters of the wood portions of the logs is about 59 mm. The average age is eleven years. The deepest penetration seemed to be in the smaller limbs The average number of rings of positive isolations is $2\frac{1}{2}$.

DEPARTMENT OF PLANT PATHOLOGY
CORNELL UNIVERSITY

NOTES ON ECONOMIC FUNGI

MEL. T. COOK

WITH TWO FIGURES IN THE TEXT

CROWN GALL ON POPLARS

During the summer of 1913 the writer's attention was called to a group of Bolleana poplars, all of which were dying. These trees, about fifty in number, had been selected because of their beauty and set along a drive

FIG. 1. Crown gall on poplars.

leading to a coach barn. They were about 30 or 40 feet in height; many of them were nearly dead and all were more or less diseased. An examination showed a great number of canker-like galls on both trunks and

branches, ranging from 5 mm. to 1 dcm. in diameter. The smaller galls were more or less spherical but, as they increased in size, tended to become flattened. The galls of previous years were dead, black, cracked and more or less decayed, but the 1913 galls were greenish white and evidently growing rapidly. They were distributed all the way from the ground up the trunk and branches to a height of 20 feet. Young galls were always found by the side of old galls, but were also found on other parts of the tree. It is very probable that the very large galls may have been the result of the union of several galls, not necessarily of the same year's growth. However, many of the distinctly single galls were 4 cm. in diameter.

Examination of the roots showed a mass of galls of various sizes and in all stages of growth and decay. Specimens were sent to Dr. Erwin F. Smith, who determined it as the true crown gall caused by *Pseudomonas tumefaciens*. There was no evidence of any other disease on these trees and it was very evident that their condition was due to this cause. The superintendent of the estate, who knew the history of the trees and the land, believed that the trees were diseased from the nursery. Whatever their condition may have been, it was very evident that they were extremely susceptible to the disease.

AN ASCOMYCETOUS FUNGUS ASSOCIATED WITH THE RHIZOCTONIA OF THE POTATO

During the past summer and fall the writer has had occasion to examine a large number of potatoes affected with various diseases. Among them were many tubers affected with Rhizoctonia, an organism which was very abundant on New Jersey grown potatoes during the past season, especially the later crop. While making these examinations, one sclerotium was found to contain a mass of well-developed asci containing spores. The number and location of the ascocarps were impossible to determine owing to the fact that the sclerotium was crushed preparatory to examination, but there were three large masses of asci and several smaller masses. The mycelium of the sclerotium was characteristic of Rhizoctonia and the asci appeared to arise directly from it, but this point could not be determined with any degree of certainty. The instruments were clean and had just been used for the examination of other sclerotia from the potatoes, which makes it impossible that the asci came from any other source. The writer immediately wrote to the man from whom the potatoes were received and secured a number of potatoes, which were examined without finding another specimen with asci. One of the laboratory assistants was

then sent to the farm to make selection of tubers notably affected with the sclerotium and these were also carefully examined with the same result.

Were these asci the fruit of a rare fungus producing a sclerotium very similar to that of *Corticium vagum* B. & C. var. *solani* Burt., or was it a case of an ascomycetous parasite growing on the sclerotium of this interesting species, or is there some other explanation of its presence? The writer will not attempt to answer the above questions but, since the diseases of the potato are attracting so much attention at this time, will present this brief note hoping that some other worker may find additional material which will be sufficient to make a contribution to our knowledge of fungi.

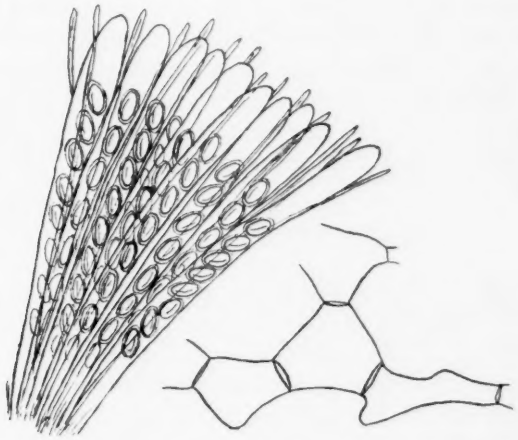


FIG. 2. Rhizoctonia mycelium from sclerotium of Corticium vagum var. solani. Cluster of asci from sclerotium (drawing by C. A. Schwarze).

PUCCINIA SUBNITENS ON THE SUGAR BEET

VENUS W. POOL AND M. B. MCKAY

WITH PLATE IX

The aecial form of *Puccinia subnitens* Diet. was observed to occur frequently during 1912 and 1913 on the sugar beet in the Arkansas Valley, Colorado, in the vicinity of Rocky Ford. As far as could be ascertained from different agriculturists the rust had been noted but once before in one locality. Dr. J. C. Arthur, in a recent letter, has noted the occurrence of this rust on the sugar beet in Colorado, but there seems to be no further reference to it in print. The increasing economic importance of this disease warrants the publication of this short report.

FORMS ON DIFFERENT HOST PLANTS

The telial form of the rust was found to occur abundantly on salt grass, *Distichlis stricta* (Torr.) Rydb (pl. IX, fig. 1), one of the common grasses along road sides where the ground was rarely or never broken. The first appearance of the aecial stage on the sugar beet was noted about the middle of May, and also at this time another aecial host of the rust, *Chenopodium album* L., was found to be heavily infected. The cotyledons (pl. IX, fig. 2) were more commonly attacked and rarely the crown (pl. IX, fig. 3) of the small beet plants. Usually one or two rust spots appeared on the cotyledons while aecia developed over the entire surface of the infected, swollen crown. No great damage seemed to result from the infection of the cotyledons since they were usually attacked too late to seriously interfere with the plant's growth. As the plant growth developed new infections appeared on the older leaves (pl. IX, fig. 4) throughout June and the first part of July. The intensity of infection then quickly diminished and the large leaves formed later, rarely developed new infection areas. Uredinia were first observed on *Distichlis stricta* early in June when the newly formed grass blades showed numerous browned areas. The telia gradually developed then in these areas until by the latter part of July the blades were thickly studded with them.

ARTIFICIAL INFECTION

Inoculations were made with the telia from the sand grass upon beets grown in the greenhouse at Rocky Ford, during the spring of 1913. Smears of teliospore material placed on the leaves of year-old beets developed few aecia. Smear inoculations on nine cotyledons yielded, after ten days incubation, three rust spots with many aecia. The teliospores in one case of stem infection had evidently been carried down the petioles to the crown where an extreme development of the rust occurred. Inoculations made on *Chenopodium album* L. at the same time yielded numerous and well developed aecia, showing that the susceptibility of this host plant was greater.

COMPARATIVE ABUNDANCE OF THE RUST IN 1912 AND 1913

During 1912 the rust was observed to occur commonly in one field and very rarely in three others. The infection seemed to be limited to the early growing period of the beet plants and occurred for the most part upon the cotyledons and crown. There was only a slight later infection on the older leaves. The infection period in these fields during 1913 continued for a longer time, and many more rust spots developed both during the early period and later on the more mature leaves. A careful survey was made of the surrounding fields together with others in the same area. Numerous rust spots were found to be developed in many of the fields although only a few leaves were attacked. The rust appeared over a much larger area and showed that under favorable conditions an infection might occur that would greatly injure the young beet plants. The close proximity of *Distichlis stricta* to sugar beet fields in certain regions would easily make this possible.

CONTROL OBSERVATIONS

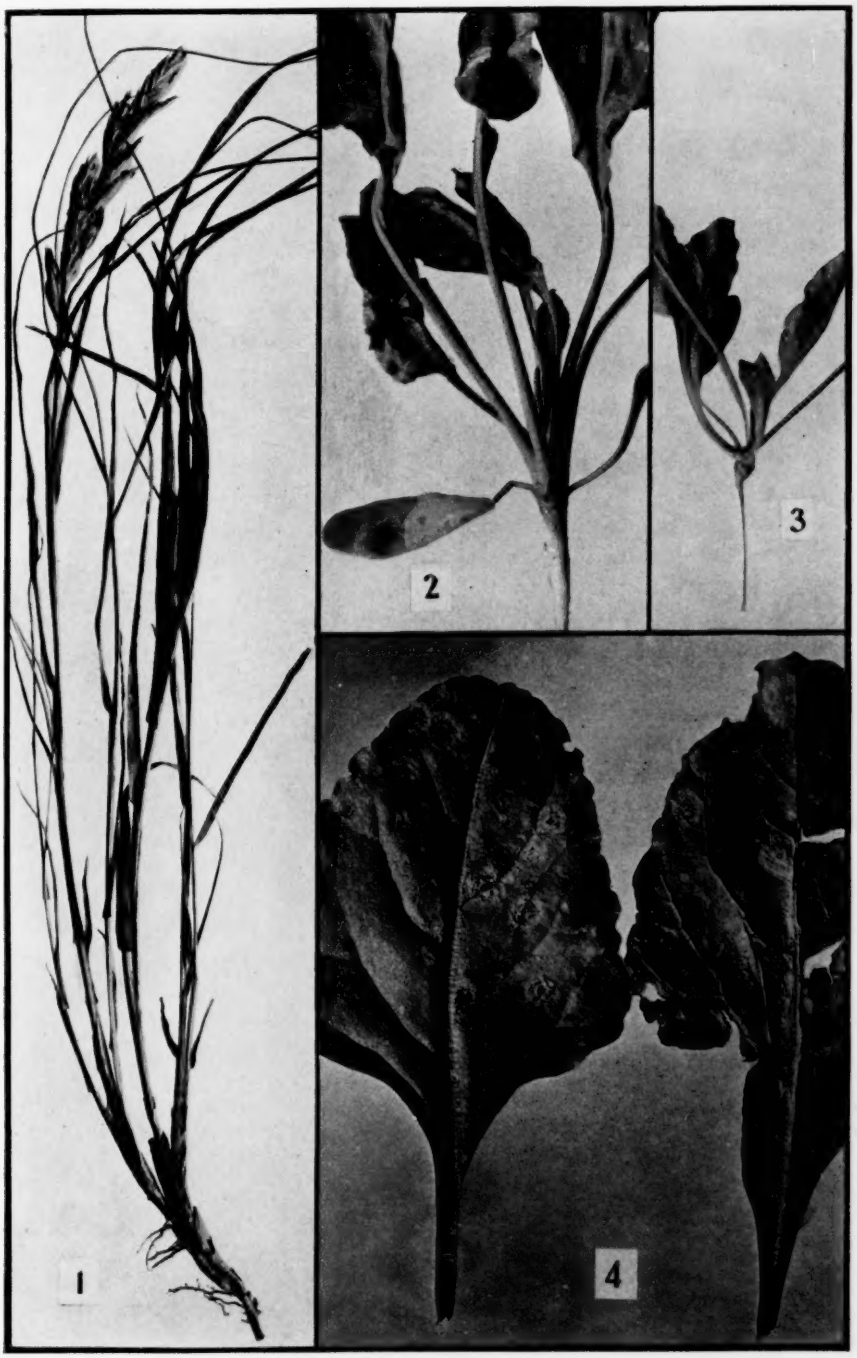
The telial form of the rust on the salt grass would be the source of infection, if at any time this disease should assume economic importance, Observations were consequently made on two different methods employed in the care of the road sides and the ditch banks, the natural habitat of the grass, with reference to their effect on the destruction of the rust. When the salt grass turf was burned over in the fall or winter much of the infected material was destroyed. Although many telia of the rust were found on the "stubble" left after burning, it is probable that the fungus is entirely killed by this method. When the turf of the salt grass was plowed under, its subsequent development was hindered greatly. This was particularly true if the plowing had been continued for several consecutive

years since a succession of grasses, as wheat and wild rye, quickly followed the plowing of the sand grass turf. However, if the ground was left undisturbed after the initial plowing, as on old ditch banks which are rarely changed, the salt grass eventually came back, pushed out the other grasses, and formed a good turf.

BUREAU OF PLANT INDUSTRY
U. S. DEPARTMENT OF AGRICULTURE

DESCRIPTION OF PLATE IX

FIG. 1. Telia on the Distichlis blades.
FIG. 2. Aecia on the cotyledons of the sugar beet.
FIG. 3. Aecia on the crown of a small sugar beet plant.
FIG. 4. Aecia on both surfaces of lower beet leaves.



POOL AND MCKAY: PUCCINIA SUBNITENS

LITERATURE ON PLANT DISEASES

INTRODUCTORY NOTE

The first installment of the list of current Pan American phytopathological literature, beginning with January 1, 1914, is given herewith as per the announcement in the last number of this journal. This will include the publications of North and South America, the West India Islands and the islands controlled by the United States, and articles by American writers appearing in foreign journals.

As the South American literature is meager, material of a more general and popular nature has been included than in the case of the North American journals. A list of the journals which have been examined regularly since January 1, 1914, is given. All publications of scientific and horticultural societies and experiment stations will, of course, be included so far as they are available in the library of the U. S. Department of Agriculture.

All authors are urged to coöperate in making this list complete by sending their separates and by making corrections and additions, and especially by calling attention to meritorious articles published in journals not in the collection of the library or not regularly examined. Reprints should be addressed to Miss E. R. Oberly, Librarian, Bureau of Plant Industry, Washington, D. C.

JOURNALS EXAMINED JANUARY 1 TO APRIL 15, 1914

The abbreviations are those used in the Experiment Station Record.

Agricultor [Merida]....Agricultor, Merida, Yucatan
Agr. News, Barbados....Agricultural News, Barbados
Amer. Bot....American Botanist, Binghamton, N. Y.
Amer. Florist....American Florist, Chicago
Amer. Jour. Bot....American Journal of Botany, Lancaster, Pa.
Amer. Nat....American Naturalist, Boston
Ann. Bot....Annals of Botany, London
Ann. Mycol....Annales Mycologici, Berlin
Bol. Soc. Agr. Mexicana....Boletín de la Sociedad Agrícola Mexicana, Mexico
Bol. Fomento, [Costa Rica]....Boletín de Fomento, San José
Bol. Sec. Agr. Cuba....Boletín Oficial de la Secretaría de Agricultura, Havana
Bot. Gaz....Botanical Gazette, Chicago
Bul. Dept. Agr. Jamaica....Bulletin of the Department of Agriculture, Kingston
Bul. Dept. Agr. Trinidad
Bulletin of the Department of Agriculture of Trinidad and Tobago, Port-of-Spain

Bul. N. Y. Bot. Gard.....Bulletin of the New York Botanical Garden
Bul. Torrey Bot. Club.....Bulletin of the Torrey Botanical Club, New York
Bul. South. Cal. Acad. Sci.
Bulletin of the Southern California Academy of Sciences, Los Angeles
Centbl. Bakt.
Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten, Jena
Jour. Agr. Research
Journal of Agricultural Research, U. S. Department of Agriculture, Wash., D. C.
Jour. Jamaica Agr. Soc.....Journal of the Jamaica Agricultural Society, Kingston
Jour. Bd. Agr. Brit. Guiana
Journal of the Board of Agriculture, British Guiana, Demerara
Jour. Heredity.....Journal of Heredity, Wash., D. C.
Jour. N. Y. Bot. Gard.....Journal of the New York Botanical Garden
Jour. Wash. Acad. Sci.....Journal of the Washington Academy of Sciences
Muhlenbergia.....Muhlenbergia, Los Gatos, Cal., etc.
Mycologia.....Mycologia, Lancaster, Pa.
Mycol. Centbl.....Mycologisches Centralblatt, Jena
Ohio Nat.....Ohio Naturalist, Columbus
Ottawa Nat.....Ottawa Naturalist
Philippine Agr. Rev.....Philippine Agricultural Review, Manila
Phytopathology.....Phytopathology, Ithaca, N. Y.
Plant World.....Plant World, Baltimore, Md.
Pomona Col. Jour. Econ. Bot.....Pomona College Journal of Economic Botany
Pop. Sci. Mo.....Popular Science Monthly, New York
Proc. Agr. Soc. Trinidad
Proceedings of the Agricultural Society of Trinidad and Tobago, Port-of-Spain
Proc. Meet. Amer. Cranberry Grow. Assoc.
Proceedings of the Meeting of the American Cranberry Growers Association, Trenton, N. J.
Rev. Agr. Salvadoreña.....Revista Agrícola Salvadoreña, San Salvador
Rev. Asoc. Rural Uruguay
Revista de la Asociación Rural del Uruguay, Montevideo
Rev. Nac. Agr.....Revista Nacional de Agricultura, Bogota
Rhodora.....Rhodora, Boston
Riv. Patol. Veg.....Rivista di Patologia Vegetale, Firenze
Rural New Yorker.....Rural New Yorker, New York
Science.....Science, New York
Torreya.....Torreya, New York
West India Com. Circ.....West India Committee Circular, London
West Indian Bul.....West Indian Bulletin, Barbados
Ztschr. Pflanzenkrank.....Zeitschrift für Pflanzenkrankheiten, Stuttgart

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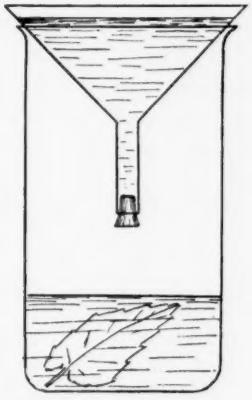
PHYTOPATHOLOGICAL NOTES

Photographing leaf spots. In attempting to make photographs of various kinds of leaves affected with leaf spots, the writer met with difficulty in obtaining the requisite contrast between the spot and the ordinary surface of the leaf. This is due to the fact that the leaf has much the same actinic value as the spot, and hence the contrast between them on the photographic plate is much less than would appear to the eye, assisted



as it is by the important factor of color. It was found that by partially extracting the chlorophyll the results obtained in the print approximated much more nearly to the normal appearance of the leaf and spot. Leaves to be photographed are immersed for a minute or two in boiling water and the surface moisture removed by blotters. They are then boiled in alcohol until they are pale enough to give the necessary contrast. If too much colour is extracted however, the leaf will look abnormally pale in the photograph. In order to prevent the alcohol from boiling away too rapidly a filter funnel, corked and filled with water, is placed in the mouth of the beaker. The cold outer surface of the funnel condenses nearly all the vaporized alcohol and returns it to the fluid below. After the requisite degree of bleaching is attained the leaves are immersed in water to get rid of the alcohol, after which blotters are again used to absorb the surface moisture. The photograph should be taken immediately as leaves treated in this way rapidly turn brown on drying.

W. A. McCubbin

For washing small objects. A cylinder of wire gauze is made so as to fit inside the lid of a small can. The lid is filled with paraffin, the cylinder inserted, and the paraffin cooled. The lid may then be removed by heating slightly, leaving a paraffin bottom in the cylinder. If set inside a crystallizing dish or other vessel of lesser height, the objects in the gauze cylinder cannot wash away and yet have a very free circulation of water around them.

W. A. MCCUBBIN

Symbols vs. terminology in ascomycetes. The value of the symbols O, I, II, III and IV as a convenient and easy method of designating the different spore forms of rusts is such that they are used by many botanists, not only in their writings, but in labeling herbarium specimens as well. To be sure very few organisms belonging to the other classes of fungi develop an equal number of spore forms in completing their life-cycle, but this fact is hardly sufficient argument for not extending, to a certain degree at least, the above mentioned simple system of designating the "stages" of many other fungi. Investigators are continually connecting up the relationship of some one or another of the imperfect fungi with their perfect stages and the proof of relationship between the non-sexual and sexual stages is today for the most part concerned with fungi of some degree of economic importance. Further, by far the greater number of imperfect fungi that have been investigated have been proven to be the non-sexual stage of some Ascomycete. In view of these facts the terminology proposed below is perhaps of greatest value when used to designate the imperfect and perfect stages extant in the life cycle of certain Ascomycetes.

For some time past the writer has made use of the numeral I to designate the non-sexual or conidial stage and II to mark the presence of the perfect stage of any ascomycetous fungus. For instance, instead of labeling our rose mildew specimens, "Odium stage of *Sphaerotheca pannosa* on cultivated Rosa" the label is written thus: "*Sphaerotheca pannosa*^{I} on cultivated Rosa," or if only the ascigerous stage occurs on the specimen to be preserved "*Sphaerotheca pannosa*^{II}." Again, we find it very convenient to designate the summer stage of Apple Scab, as *Venturia inequalis*^{I} on, etc." Likewise, "*Podosphaera oxyacanthae* $^{I \& II}$" shows us that the specimen so designated has upon it both the conidial and ascigerous stages. Why continue to use "gleosporial stage," "monilial stage," "pycnidial stage," "conidial stage," etc., when the numeral "I" along with the accepted name of the ascigerous stage (the correct name of the fungus) may be used instead?

H. M. JENNISON

A snapdragon wilt due to Verticillium. A new wilt of the cultivated snapdragon has been prevalent the past year among plants grown in greenhouses as well as those grown out of doors. This wilt is not restricted to any particular section of the United States, for florists have reported it from the East and from the West. It occurred last summer in the gardens of the Department of Agriculture at Washington, D. C., and in the Department greenhouses this winter.

Some of the plants in the greenhouses affected with this wilt were given me for inspection. I found fungous hyphae in the vessels, isolated a Verticillium from these plants and reproduced the disease by inoculation with the fungus isolated.

NELLIE A. BROWN

Dr. Schoene and Mr. Price, of the Virginia Crop Pest Commission, have brought me from Abingdon and other points in southwest Virginia, apple limbs infested with San José scale which had been parasitized by *Sphaerostilbe coccophila.* All of the insects had been killed and one or more of the red conidiophore bundles of the fungus protruded from under the armor of each. Pure cultures were obtained and placed in stock. The economic value of this fungus as a scale destroyer is probably small in most localities but at the high altitude of southwest Virginia with its heavy precipitation and its dewy summer nights it appears to be a common and efficient scale parasite.

C. H. CRABILL

Personals. Mr. Alfred S. Orcutt, formerly a graduate student majoring in plant pathology at the University of Wisconsin, has accepted a position as assistant in the department of botany of the Ohio Agricultural Experiment Station.

Dr. H. W. Wollenweber, of the Bureau of Plant Industry, sailed on December 2, 1913, for Europe, where he will be engaged in investigating potato diseases and in completing his monograph of Fusarium by studying in the leading European herbaria.

Dr. H. A. Edson, of the Bureau of Plant Industry, sailed on March 24, 1914, for Germany, where he will spend several months in the study of sugar beet root-rot and damping-off diseases and in work on a monograph of Rhizoctonia.

Bitter rot of apples in the Pacific Northwest. The apple anthracnose fungus, *Neofabrea malicorticis* (Cord.) Jack., has been thought to cause the rotting of apples in storage, so extensive at times in western Washington. Since the methods of controlling this disease on the Station farm, coupled

with the weather conditions last fall, were such that the amount of rotting which appeared in storage was far greater than was felt to be warranted under the circumstances, a close watch was kept on stored apples in an effort to determine whether any other fungus might be causing the rot. Early in October apples were found with rotted areas, the pycnidia being arranged on these areas in a more concentric manner than is usually the case with apple anthracnose. The fungus was isolated and York Imperials and Baldwins were inoculated, wrapped and stored in a cool cellar in a place where apples had never before been stored. Rotting commenced eleven days after inoculation, and pycnidia appeared within eighteen days. Later it became apparent that the fungus in question was *Glomerella rufomaculans*, as had previously been suspected. All of the gross characteristics noted by Burrill and Spaulding and von Schrenk were present, and sections of the pycnidia were like those pictured by Hasselbring and Burrill. Setae did not appear, however, until six weeks after inoculation. Spores usually became 1-septate upon germination and the formation of appressoria was constant. Perithecia have not been formed as yet on six months old potato-dextrose-agar cultures.

The similarity of the gross characteristics of the imperfect stages on the fruit of the bitter rot fungus and the anthracnose fungus indicates the possibility of the previous confusion of these two. In the writer's observations a microscopical observation has always been necessary for a positive identification.

Both species bear their spores in the same manner. The spores of both are also similar and may be either straight or curved. The anthracnose spores, however, are usually more constant in this characteristic. The bitter rot spores always possess blunt, rounded ends, with the walls parallel, while the anthracnose spores are always elliptical, with the walls tapering to more or less of a point at the ends.

The bitter rot fungus has not been positively identified as causing any of the cankers on apple trees, but the similarity of the anthracnose cankers to those caused by the bitter rot fungus as noted by those familiar with the latter, leads the writer to suspect that the causes of the cankers as well as of the fruit rots may be confused. Over a year ago while connected with the Oregon Experiment Station the writer proved the pathogenicity on apple bark and fruit of several fungi not previously described as occurring in Oregon and not as yet identified. The similarity of some of these forms with the bitter rot fungus, together with observations made by the writer both in Oregon and Washington, lead him to suspect that the bitter rot disease occurs also in Oregon.

The writer has been unable to find any reference in literature regarding the occurrence of this disease on the Pacific Coast, and a letter from Profes-

sor Brooks of the Office of Fruit Disease Investigations, U. S. Department of Agriculture, states that that office contains no record of any report of the occurrence of *Glomerella rufomaculans* on the Pacific Coast.

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